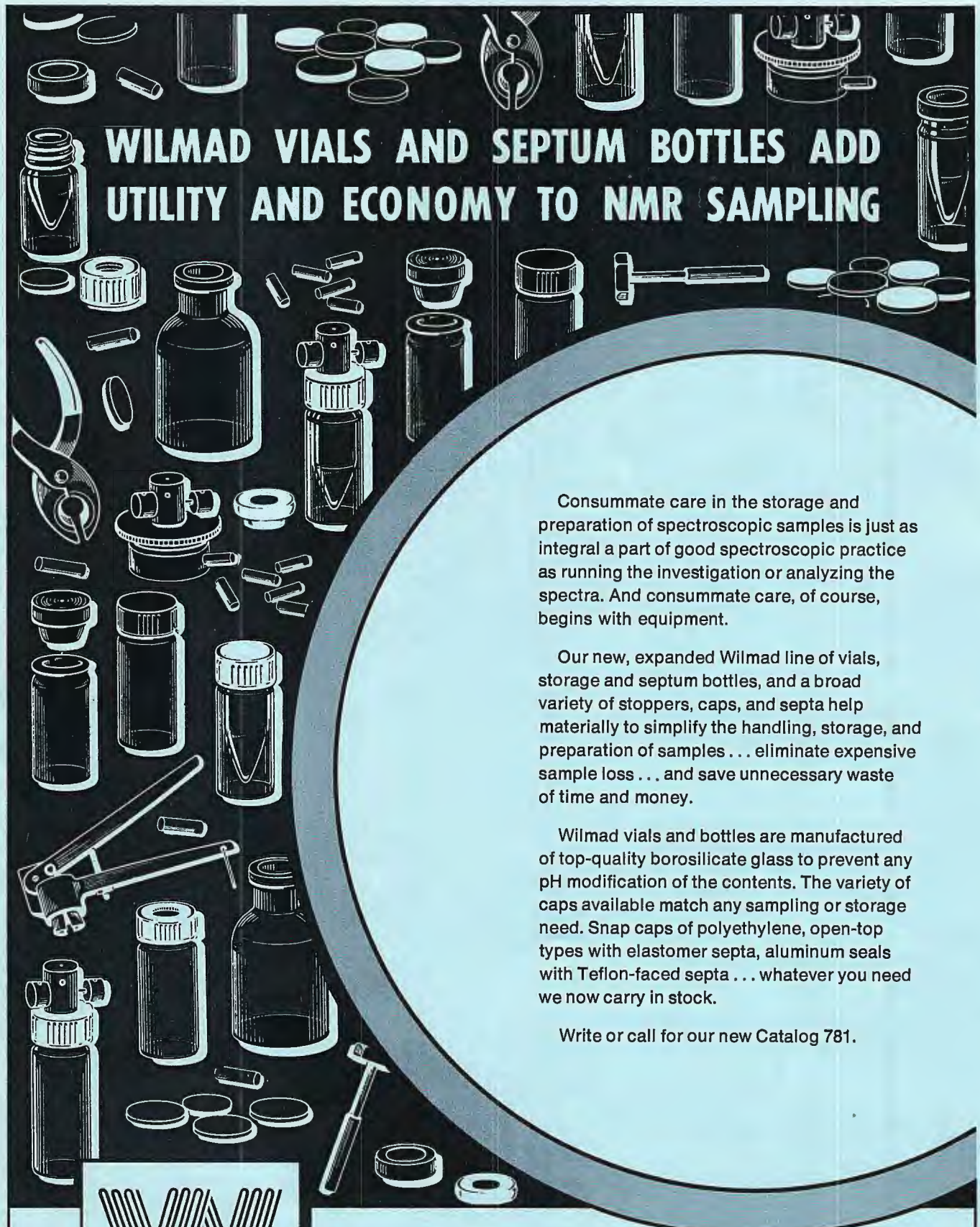
Texas A & M University
N - M - R
Newsletter

No. 245

February, 1979



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DEADLINE DATES: No. 246: 5 March 1979
No. 247: 2 April 1979

All Newsletter Correspondence, Etc. Should Be Addressed To:

Dr. Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843 U.S.A.

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 245

INDIANA UNIVERSITY
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TEL. NO. 812—337 5513

January 9, 1979

Professor B. L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas

Dear Barry:

Studies of the Carbohydrate Residues of Glycoproteins by Natural-Abundance Carbon-13 NMR

The determination of the structures of the carbohydrate residues of a glycoprotein, traditionally carried out by enzymatic and chemical procedures, is usually a task of major magnitude. My co-worker, Dr. Kilian Dill, has studied the feasibility of applying ^{13}C NMR to studies of glycoproteins. He has obtained information about the structure and mobility of the carbohydrate residues of the glycoprotein glucoamylase (from Aspergillus niger). Also, his results yield information about the applicability and limitations of ^{13}C NMR spectroscopy for studies of glycoproteins in general. We believe that this is the first study that deals with the interpretation of ^{13}C NMR spectra of glycoproteins.

Aspergillus niger produces two forms (isoenzymes) of glucoamylase, designated glucoamylase I and glucoamylase II on the basis of their electrophoretic mobility. The molecular weights of glucoamylase I and glucoamylase II are about 100,000 and 110,000, respectively. The two isoenzymes possess indistinguishable amino acid compositions, and, presumably, identical amino acid sequences, each with about 800 amino acid residues.

The ^{13}C resonances of all anomeric carbons and most non-anomeric carbons of the carbohydrate residues do not overlap with the resonances of amino acid residues. Measured T_1 and NOE values indicate that it is feasible to use peak intensities for quantitative determinations of carbohydrate residues. A comparison of the spectra of native and denatured glucoamylase reveals that the ^{13}C resonances of many amino acid residues of native glucoamylase exhibit the chemical shift nonequivalence (caused by protein folding) previously observed for unglycosylated globular proteins. In contrast, the ^{13}C resonances of most carbohydrate residues are not significantly affected by protein folding: Spectra of denatured and native glucoamylase yield very similar patterns of narrow resonances of carbohydrate residues. This result is consistent with the expected solvent exposure of the

carbohydrate residues, and with evidence (based on T_1 and NOE values) for fast internal motions of these residues. Published chemical shifts of carbohydrates were used to assign the carbohydrate resonances of glucoamylase. Integrated intensities indicate an average of about 120 carbohydrate residues per molecule (in our mixture of the two isoenzymes of glucoamylase). There are about 80 α-D-mannopyranose residues, about 10 α-D-glucopyranose residues, and a maximum of 15 (if any) β-D-mannopyranose residues. Hexosamine residues are not detected. All of the observed 120 carbohydrate residues must be involved in glycosidic linkages (to serine, threonine, or carbohydrate residues); there are no strong resonances assignable to carbohydrate residues involved in glycosylamine linkages (to asparagine or glutamine residues). It is likely that most or all of the α-D-glucopyranose residues are linked to the same type of carbon (of serine, threonine, or mannose residues). In contrast, the anomeric carbons of the α-D-mannopyranose residues participate in various types of glycosidic linkages, about 30 of which probably involve Carbon 2 or 3 (or some of each) of other α-D-mannopyranose residues. We rule out the possibility that most of the α-D-mannopyranose units are single residue side chains. All of the above observations are consistent with, but significantly extend, previous knowledge about the carbohydrate residues of A. niger glucoamylase.

Preprints are available upon request.

Sincerely,

Adam

Adam Allerhand
Professor and Chairman

245-3

VRIJE UNIVERSITEIT

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Professor Barry Shapiro
Department of Chemistry
Texas A & M University
College of Science
College Station, Texas 77843
U.S.A.

uw kenmerk	uw brief van	ons kenmerk	datum	bijlage(n)
		CM/IS	January 3, 1979	

onderwerp

Dear professor Shapiro,

In our laboratory we have been studying NMR spectra of partially oriented molecules for a number of years. Up to now the alignment was obtained by using liquid crystals as a solvent or by means of orienting electric fields.

Recently we have detected a new orienting mechanism. When magnetically anisotropic molecules are placed in a strong magnetic field they tend to align with the largest component of the susceptibility tensor parallel to the external field. The resulting alignment for molecules with a magnetic susceptibility anisotropy of around 10^{-28} e.m.u. in a magnetic field of say 10 Tesla is five to six orders less than in a thermotropic liquid crystal.

Nevertheless, the above alignment is detectable in the ^{2}H NMR spectrum, giving rise to a splitting of about one Hz. This splitting originates from the interaction of the nuclear quadrupole moment with the surrounding electrons. In the case of deuterium the quadrupole coupling constant is large enough to generate a measurable line splitting, whereas it is not so large as to obscure it by line broadening due to quadrupolar relaxation.

We have detected these splittings in the 61.42 MHz spectra of some deuterated aromatic hydrocarbons (1) and report now a rather large effect on the ^{2}H signal from perdeuterocoronene, as shown in the figure. The spectrum has been recorded on a Bruker WH 400 spectrometer of Spectrospin in Zürich, operating at 9.3 T.

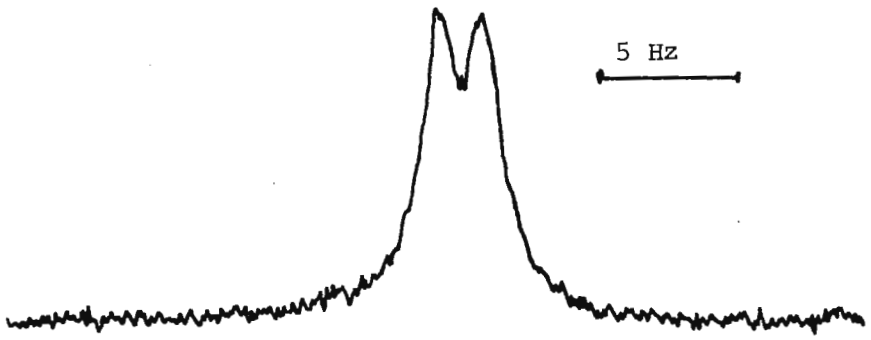
By superposing two lorentzian lines the splitting is analyzed to be 1.4 Hz. From this the anisotropy in the magnetic susceptibility may be calculated and is found to be 3.8×10^{-28} e.m.u..

The effect described offers a new method to study the diamagnetic susceptibility tensor and its dependence on molecular interactions. The information can in principle also be deduced from T_2 experiments. On the other hand it should be taken into account when deriving T_2 values from linewidths.

Sincerely,

(J.A.B. Lohman) (C. MacLean)

(1) J.A.B. Lohman and C. MacLean, Chem. Phys., 35, 269 (1978); Chem. Phys. Lett. 58, 483 (1978).



61.42 MHz ^{2}H NMR spectrum of perdeuterocoronene

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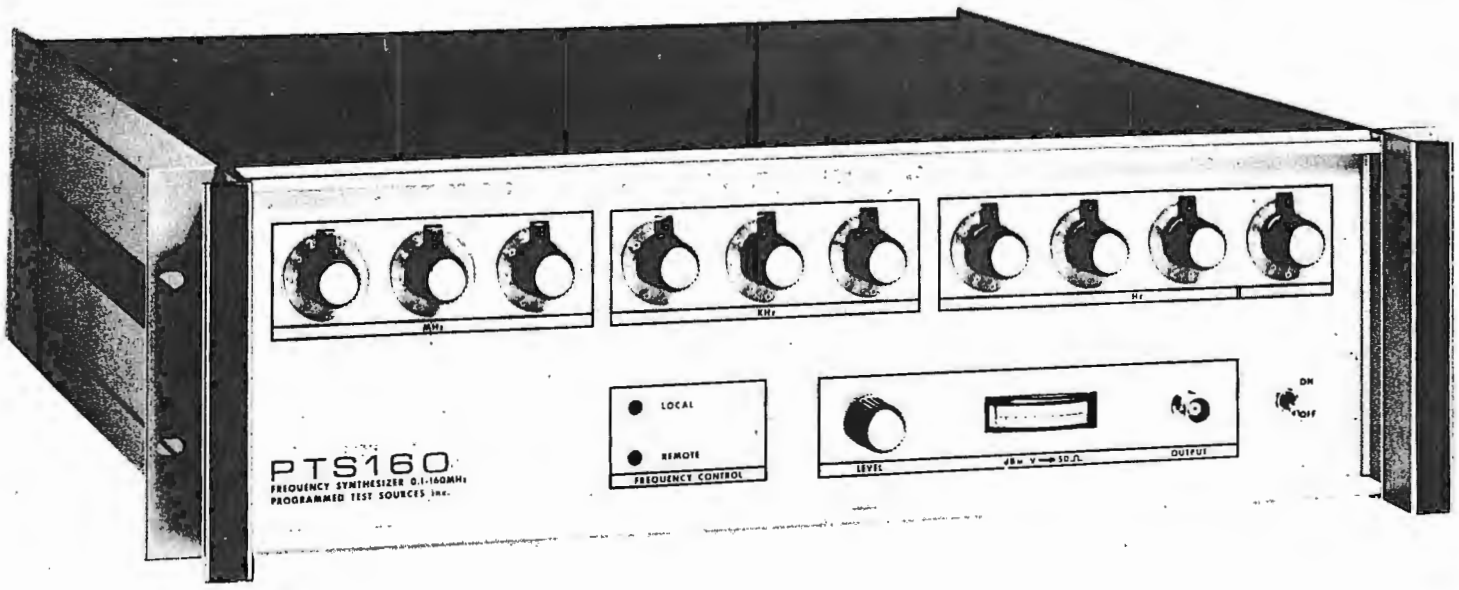

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The University of Alabama in Birmingham
Comprehensive Cancer Center

December 27, 1978

Professor Bernard L. Shapiro
Department of Chemistry
College of Sciences
Texas A & M University
College Station, Texas 77843

"Transfer of Magnetization as a Method For Measuring the Kinetics of Dissociation of Metal Complexes"

Dear Barry:

For the past two years, we have been characterizing the various metal complexes of the water-soluble glycopeptide antibiotic bleomycin(1). (see Figure 1). In the course of ^{1}H NMR investigations of the Zn(II) complex, we found that at room temperature, several protons in bleomycin were in slow exchange (on the ^{1}H NMR chemical shift time scale) between their free and complexed states.

The aromatic region of the 360 ^{1}H NMR spectrum of bleomycin in the presence of Zn(II) is shown in Figure 2a. The spectrum obtained on the complete saturation of the C2 proton of the Zn(II)-bleomycin complex is shown in Figure 2b. Note the significant decrease in intensity in the C2 resonance of the free bleomycin. When the frequency of the decoupler was shifted to 7.4 ppm, the spectrum obtained was identical to that shown in figure 2a. These experiments were repeated at several different temperatures ranging from 303°K to 353°K. As expected, the extent of saturation transfer was strongly temperature dependent, ranging from 0.06 at 303°K to 0.84 at 353°K.

Transfer of saturation is governed by equation (1):

$$(M_0^\alpha - M_z^\alpha)/M_0^\alpha = [T_{1_\alpha}/(T_{1_\alpha} + \tau_\alpha)]\ [(M_0^\beta - M_z^\beta)/M_0^\beta], \qquad (1)$$

which was derived from modified Bloch equations using a procedure analogous to that used by Gupta and Redfield (2). The α and β states refer to two nuclei which are chemically exchanging. T_1, τ_α, M_z^α and M_0^α are the spin-lattice relaxation time, life time, observed magnetization and equilibrium magnetization of the α nucleus, respectively. Analogous notation is used for the β nucleus. $(M_0^\alpha - M_z^\alpha)/M_0^\alpha$ is the fractional decrease in resonance intensity of the α resonance resulting from the double irradiation of the β resonance, whose intensity is diminished by a factor of $(M_0^\beta - M_z^\beta)/M_0^\beta$.

Comprehensive Cancer Center

December 27, 1978

Complete saturation of the β state causes a fractional decrease of the α resonance equal to $T_{1\alpha}/(T_{1\alpha} + \tau_\alpha)$, which is significant only if the pseudo-first order rate constant for exchange of the α nucleus $1/\tau_\alpha$, is comparable to or greater than its relaxation rate, $1/T_{1\alpha}$. Since the quantitative analysis of the transfer of saturation experiments required a knowledge of the T_1's of the free bleomycin peaks, we measured these parameters at several temperatures between 303°K and 353°K. Using these results in equation 1, we obtained values for τ, the exchange lifetime, at the various temperatures. Note that this τ is the lifetime of bleomycin in its free or uncomplexed state. From the McConnell development, the lifetimes of the free and bound states are related by

$$\tau_B = (P_B/P_F)\ \tau_F\ , \qquad (2)$$

where P_B and P_F are the fractional populations in the bound and free states, respectively, these values can be determined by measuring the integrated intensities of the appropriate peaks in Figure 2a. In this manner, it is possible to determine τ_B, the lifetime of the bleomycin molecule in the complexed state. It is often assumed that the mechanism for the dissociation step of metal complexes is first order. A result of this assumption is that τ_B is a characteristic of the system and its inverse is a true rate constant. From an Arrhenius plot we determined that the energy of activation for the dissociation of the complex was 16.2 Kcal with an entropy of activation of ca 50 eu. We suggest that the approach outlined here might be of some interest in studying other systems which are in the slow exchange region.

Sincerely,

Bob Jerry

R.E. Lenkinski, J.L. Dallas

REL:JLD/tc

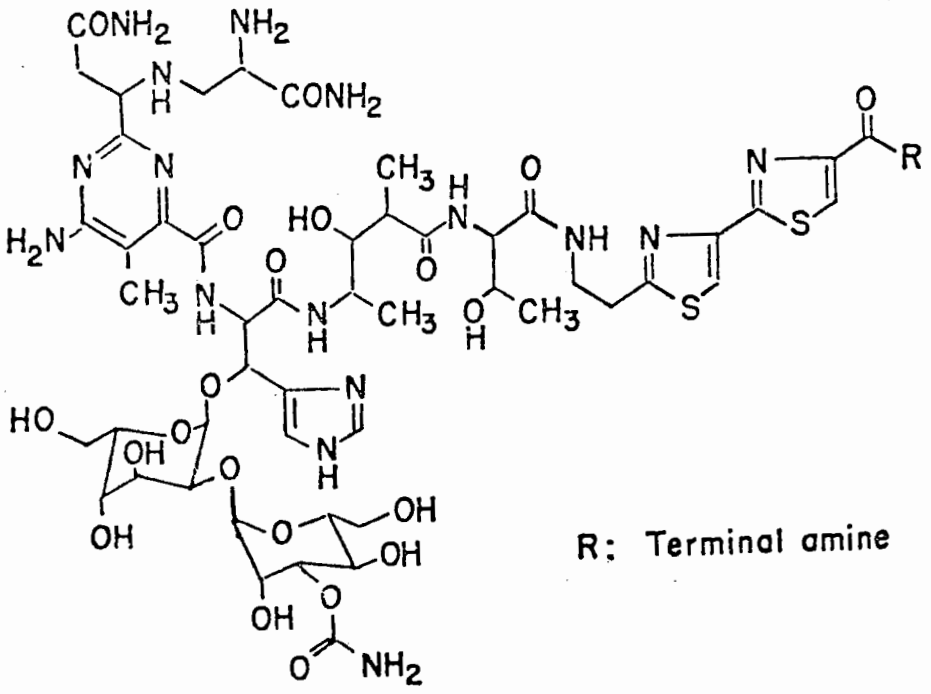
cc

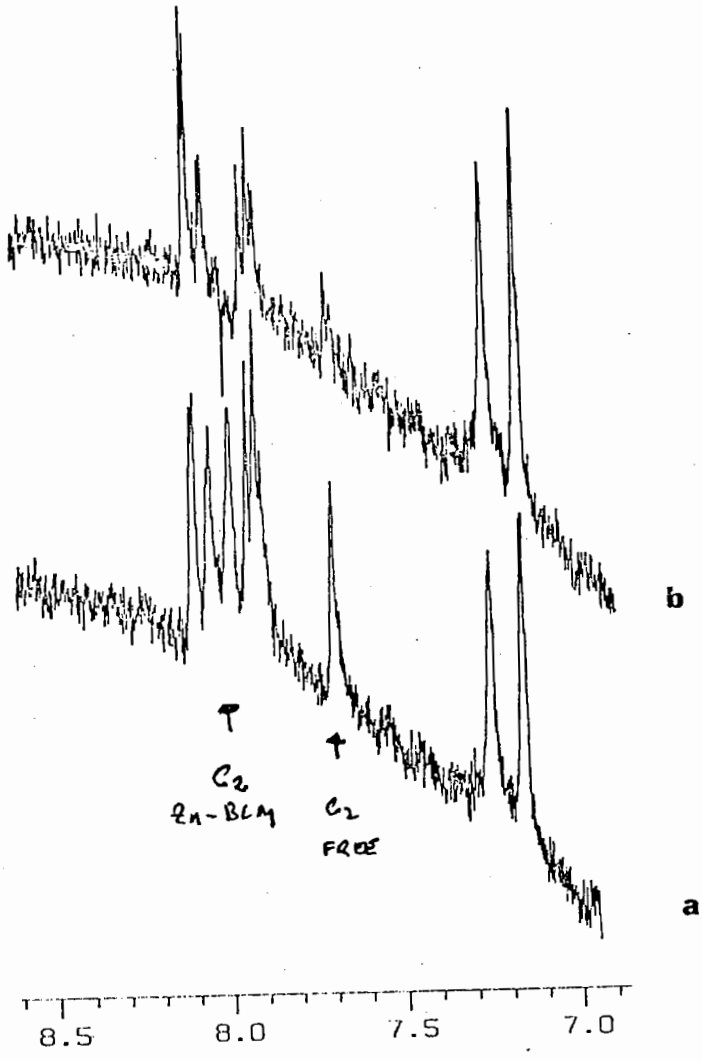
(1) For a review see: S.T. Crooke and W.T. Bradner, Journal of Med. 7, 333(1977).

(2) R.K. Gupta and A.G. Redfield, Biochem. Biophys. Res. Commun. 41, 273(1970).

Structure of bleomycin

Comprehensive Cancer Center





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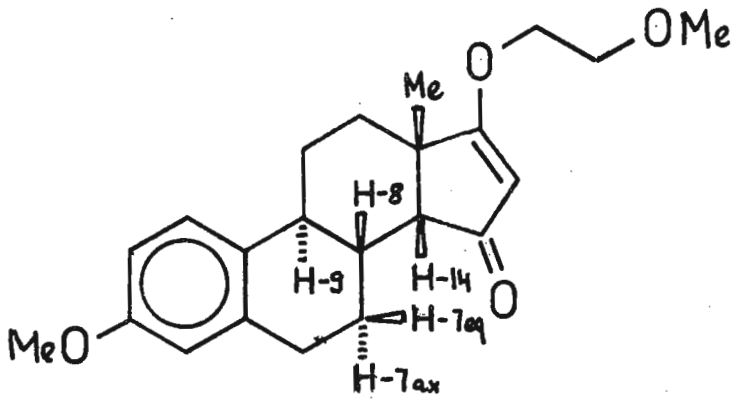
Prof. B.L. Shapiro
Department of Chemistry
Texas A & M University
College of Science
COLLEGE STATION
Texas 77843
U.S.A.

A HOMONUCLEAR SPI EXPERIMENT

-6. JAN. 1979

On a recent visit to Bruker-Physik in Karlsruhe I persuaded Dr Formacek to do a homonuclear SPI experiment for us on their WP-200 spectrometer to determine the stereochemistry of the steroid derivative (1)



(1)

The 200 MHz proton spectrum of (1) was rather complex but showed the H-14 signal as a well defined doublet at $\delta \approx 2.5$. Inversion of one of these lines should affect the intensities of the H-8 transitions and reveal all couplings involving H-8.

The required pulse sequence[1,2] (selective π-pulse at exact frequencey of line to be inverted, non-selective $\pi/4$-pulse, data acquisition, delay time) was easily programmed. The inherent stability of a superconducting spectrometer system allowed us to repeat the sequence several times, store the Fourier-transformed spectrum and execute the same sequence with the selective pulse placed outside the range of the proton resonances to obtain the unperturbed spectrum. Subtraction of the two spectra resulted in the INDOR-like signal shown in the Figure. The expected 16 lines were reduced to a 12-line signal due to the accidental equivalence of two couplings.

In addition to the (H-8, H-14) coupling of 5.5 Hz, proton H-8 shows two large *trans* diaxial couplings of 12 Hz and a small coupling of 2.5 Hz. This confirms the *trans* B/C ring junction and establishes the conformation of the B-ring.

Best regards

Yours sincerely

K. Pachler
HEAD : PHYSICAL CHEMISTRY DIVISION

References

(1) K.G.R. Pachler, P.L. Wessels, J. Magn. Resonance 12, 337 (1973)

(2) K.G.R. Pachler, P.L. Wessels, J.C.S. Chem. Comm. 1974, 1038

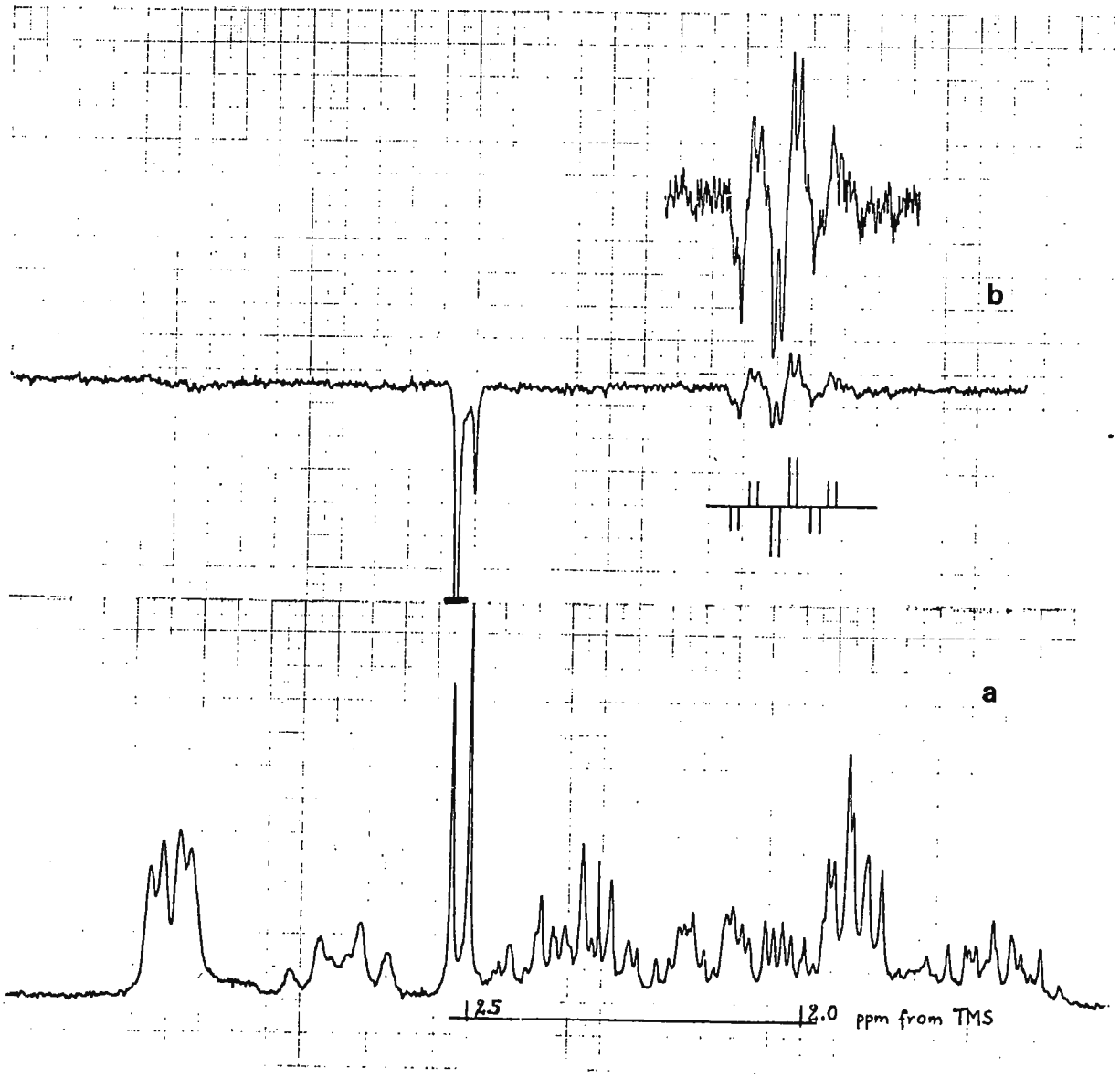


Figure:

(a) Relevant part of the 200 MHz proton spectrum of compound (1)

(b) Result of the SPI experiment, displayed in the difference mode.

Note the near-perfect cancellation of the entire spectrum except for the inverted transition, a slight decrease of the other doublet line, and the positive and negative peaks of the H-8 pattern.

The S/N ratio could easily be improved by increasing the number of transients.

University of Bristol School of Chemistry

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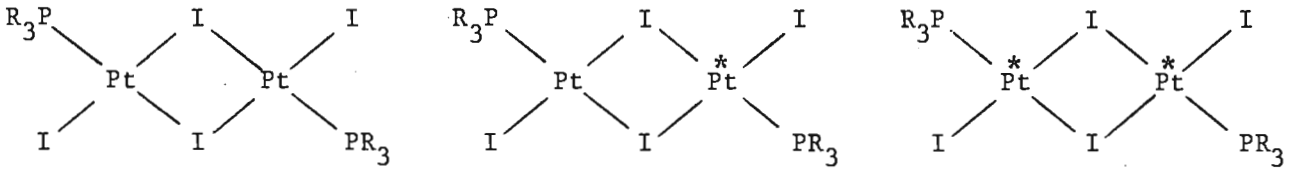
Professor Bernard L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station,
Texas 77843,
U.S.A.

10th. January, 1979.

Dear Professor Shapiro,

Isotopic Isomers? - Wide Spectra.

Whilst Dr. Haigh's letter showed how to use Polya's theorem to obtain the number of different isotopic species (Newsletter 233 - 9) it still left (me, at least) the problem of what to call them. If I follow that contribution correctly, the term 'isotopic isomer' was used to describe species differing in the number of ^{29}Si nuclei as well as those differing in the arrangement of the same number of ^{29}Si's. The term 'magnetic isomer' has also been used e.g. to describe:-



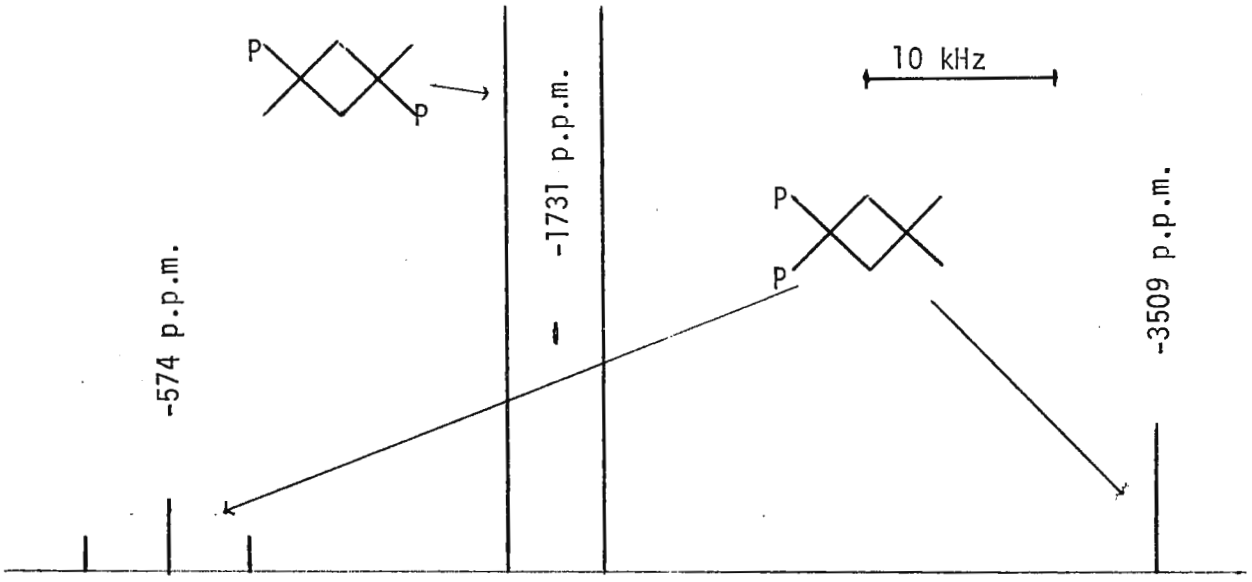
where Pt^* is ^{195}Pt with $I = \frac{1}{2}$ and the others have $I = 0$. Martin Murray here pointed out that the use of 'isomer' is not really appropriate in cases where the number of a particular isotope varies since the usual definitions of isomers are that they have the same (%) composition and molecular weight. Of course the deviations are relatively small for isotopes of Si and Pt, but would be major in the case of hydrogen e.g. I - III which might be found in a bottle of not very good deuterio-acetone.

$CD_3CO.CD_3$(I) $CD_3CO.CD_2H$(II) $CD_3CO.CDH_2$(III) $CD_2HCO.CD_2H$(IV)

As the terminology should be equally applicable to all cases some other word or phrase seems to be needed with, perhaps, the retention of 'isotopic isomers' to describe the different distributions of the same set of nuclei e.g. III and IV. I have used 'isotopomer' which I thought I saw somewhere but now I am uncertain where or whether it is the correct term. I have asked our organic chemists who are much better at nomenclature etc and our Mass Spectroscopists who calculate isotopic distributions but they could not help. Can any Newsletter reader give me assistance on this point which will become more important with the increased use of multinuclear systems?

Whilst not as dramatic as their EPR example, I can provide Eaton and Eaton (Newsletter 234-4) with an n.m.r. example of an [AB] pattern which should show a measurable difference between field and frequency sweep spectra. The compound is $[(cod)Pt\{C(CF_3)_2O\}Pt(cod)]$ (cod = cyclo-octa-1,5-diene) which we measured by ^{19}F-$\{^{195}Pt\}$ INDOR (Boag et.al. J.Chem.Research 1978,(S) 228, copies of full text version available from me). The chemical shifts of the two ^{195}Pt nuclei are 190 and 824 p.p.m. to high frequency of $\Xi(^{195}Pt)$ = 21.4 MHz and for the species with two ^{195}Pt's, J(PtPt) is + 5355 ± 10 Hz. At 2.34T, I calculate D, the difference in the splittings (N.V. Riggs, Newsletter 234-3) to be 3.2 Hz with D/J = 0.0006 (ignoring all the protons and fluorines, of course). On the more practical side, the outside lines are very nearly 20 kHz apart - something to be borne in mind when purchasing new spectrometers with the intention of using a multinuclear system to study heavy metal resonances especially in the case of supercon's.

Two other examples of wide spectra come from a recent, very satisfactory, session at JEOL(UK) with Peter Beynon running ^{199}Hg spectra on their FX 100Q fitted with a multinuclear probe. Mixtures of mercuric halides with mercuric cyanide showed the resonances of Hg(CN)X as well as those of HgX_2 and $Hg(CN)_2$ at room temperature in contrast to a mixture of $HgCl_2$ and $HgBr_2$ which we were unable to 'stop'. For HgI_2/Hg(CN)I/$Hg(CN)_2$ in tetrahydrofuran the shifts were -3430, -1942, and -1386 p.p.m. to high frequency of neat dimethyl mercury, equivalent to a range of 36.6 kHz. (The other shifts were $HgCl_2$, -1549; Hg(CN)Cl, -1434; $HgBr_2$, -2209; Hg(CN)Br, -1615 p.p.m.). These are part of an n.m.r. study of linear mercury complexes which has been submitted to J.Chem.Research, copies of full text available on request. The spectrum of $[Hg_2I_4(PBu^n_3)_2]$ which exists as two isomers, was even wider and as the largest frequency range on this particular instrument was 20 kHz we had to measure the spectrum in three portions!



Yours sincerely,

Robin Goodfellow

R. J. Goodfellow

University of Illinois at Urbana-Champaign

School of Chemical Sciences
148 Roger Adams Laboratory
Urbana, Illinois 61801

January 11, 1979

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Dr. Shapiro:

In response to pink slip demands, we would like to give an interim report of one of our instrumental updating projects in the Molecular Spectroscopy Lab here at Illinois. Our aim has been to increase the performance of our XL100 through both probe improvement and convenient multinuclear operation. Because of the various "birdies" seen from the XL console, the aim of our modifications is to eventually retire it from service.

Initially, we constructed a 12 mm, ^{13}C probe to replace the Varian 4412 probe. The Varian preamps we replaced with wideband, low noise preamps (Amplica and Miteq). The coil arrangement consists of a 10 turn, 20 mm long transmit/receive coil wound on the inside of a glass coil support. On the outside of the glass support was wound a 2 turn Helmholtz coil. This coil was doubly turned for both lock (15.4 MHz) and decoupling. The S/N performance on our probe was 70:1 for 80% dioxane (coupled, one 90° pulse, 1.5 Hz line broadening) vs. 25:1 for the Varian 4412 probe, however, much of this increase can be attributed to the greater length of our coil. After evaluating a number of capacitors for tuning and matching, we are currently using JFD 0.8-30 pf capacitors. These enable us to achieve a frequency range from 22-41 MHz.

Using a frequency synthesizer to generate the necessary observe frequencies, we have constructed a spectrometer to observe resonances in the above range. The accompanying figure gives a schematic representation of our spectrometer. So far we have observed ^{11}B, ^{23}Na, ^{55}Mn, ^{59}Co, ^{127}I, ^{13}C and ^{31}P. As the Varian decoupler proved to interact too strongly with the lock channel, we threw together the noise modulated decoupler shown in the figure. We found this decoupler to cause no problems with the lock.

We have found our system to be low cost (about $4000, without synthesizer), free of many of the "birdies" seen with the XL100 console, and yielding greater performance.

We plan ultimately to cover the frequency range from ca. 6 to 41 MHz and to have probes for 2 mm, 12 mm, and 22 mm tubes.

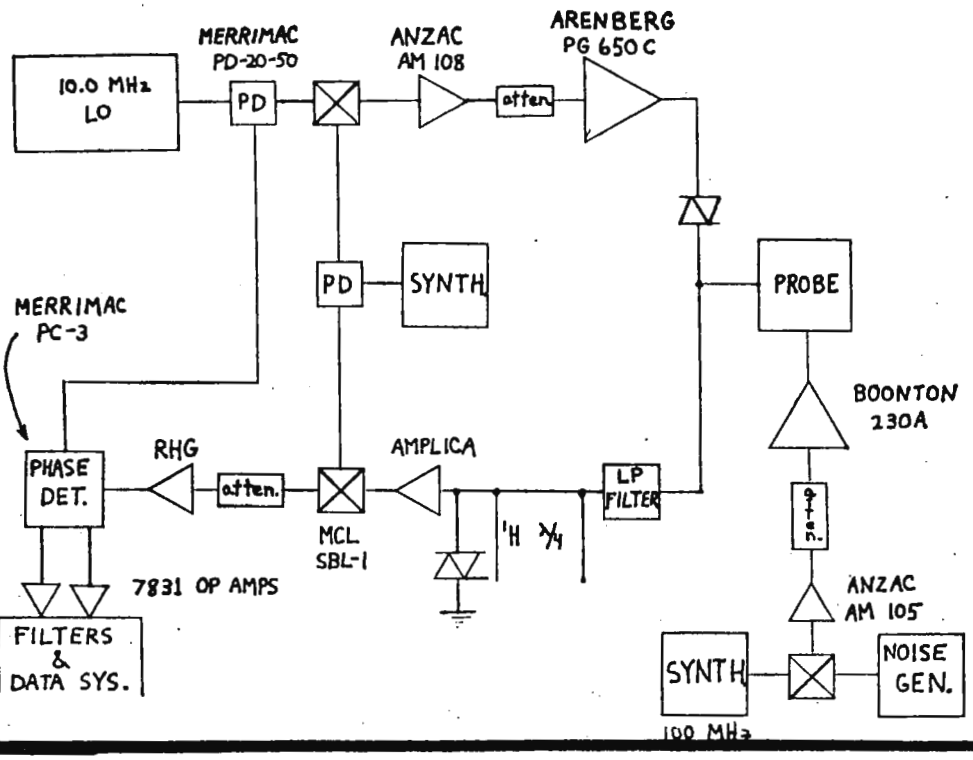
Sincerely yours,

Bruce J. Williams
Bruce J. Williams

David A. Wright
David A. Wright

Stephen E. Ulrich
Stephen E. Ulrich

SEU/pw



the University of Alabama in Birmingham / UNIVERSITY STATION / BIRMINGHAM, ALABAMA 35294

January 24, 1979

A postdoctoral position is available in our laboratory for a recent Ph.D. with experience in nmr spectroscopy interested in developing nmr techniques for delineating the solution conformation of peptides. The project will employ the neurohypophyseal hormones, oxytocin and vasopressin, as the principal models. The project will stress multiple resonance experiments (e.g., NOE and transfer of saturation) and paramagnetic probe techniques. Available instrumentation includes Bruker WH-400, CXP-270 and HX-90 spectrometers.

The preferred starting date is February - June, 1979. The salary is $10,000 plus fringe benefits. Please have appropriate candidates contact me.

Sincerely yours,

Jerry D. Glickson

Jerry D. Glickson, Ph.D.
Director, Cancer Center,
NMR Core Facility

University of Waterloo

Waterloo, Ontario, Canada
N2L 3G1

Faculty of Science
Department of Chemistry
519/885-1211

Dec. 28,1978

Dr. Bernard L. Shapiro
Texas A&M University
College of Science
Department of Chemistry
College Station, Texas 77843

Dear Barry:

Subject: ^{2}H NMR of Dipalmitoyl Lecithin and Palmitic Acid Guests in a Magnetically Oriented Liquid Crystalline System.

The membrane phospholipid, dipalmitoyl lecithin, deuterium labelled in its fatty acyl chains, and palmitic acid-d_{31} have been incorporated into the same bilayer model membrane, a lyotropic liquid crystalline hexadecyltrimethylammonium bromide mesophase which spontaneously orients in an applied magnetic field. The order parameter profiles for the lecithin and palmitic acid, and that of the host detergent are quite different indicating that the ordering of the incorporated lipids is not dictated by surrounding detergent molecules, but rather the order imposed is a function of the nature of the chemical anchoring of the hydrophilic headgroups of the individual molecules at the bilayer interface.Dissimilarities in the order profiles may be interpreted in terms of variations in the ease of formation of random gauche conformers along the length of the acyl chains. In addition, the validity of the use of perdeuterated fatty acids as probes of the order of other membrane components is questioned.

For the Host detergent, the relaxation rate $^{1}/T_{2}$ obtained from the line width is directly proportional to the deuterium quadrupole splitting of the $-CD_2-$ segments for that flexible part of the chain beyond the plateau region of constant degree of order.

Please credit this submission to the account of Dr. L.W. Reeves, as he is presently in Brazil.

Sincerely,

Bruce

Bruce J. Forrest

Prof. Dr. Horst Kessler
Institut für Organische Chemie
der Johann Wolfgang Goethe-Universität
Frankfurt am Main

January 9, 1979

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Professor Bernard L. Shapiro
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U.S.A.

German NMR Spectroscopists organized in the "Fachgruppe Magnetische Resonanzspektroskopie" in the "Gesellschaft Deutscher Chemiker"

Your pink letter reminds me about my "duty". The reason for my delay is mostly due to our move into another location (new adress!).

I will focus your interest to the fact that the former German NMR Discussion Group is now organized in the "Fachgruppe Magnetische Resonanzspektroskopie" in the German Chemical Society. The foundation and the election of the board was at the 5th meeting of the German NMR Discussion Group in Ettal (Chairman: G. Binsch, also see TAMU-NMR Newsletter 238, 16 (1978)).

The members of the board are:

H. Kessler, Frankfurt, University (chairman)
W. Bremser, Ludwigshafen, BASF (vice-chairman)
F. A. Neugebauer, Heidelberg, University
D. Ziessow, Berlin, Technical University
D. Leibfritz, Bremen, University
H. Günther, Siegen, University

If anyone is interested in more information, please, contact me.

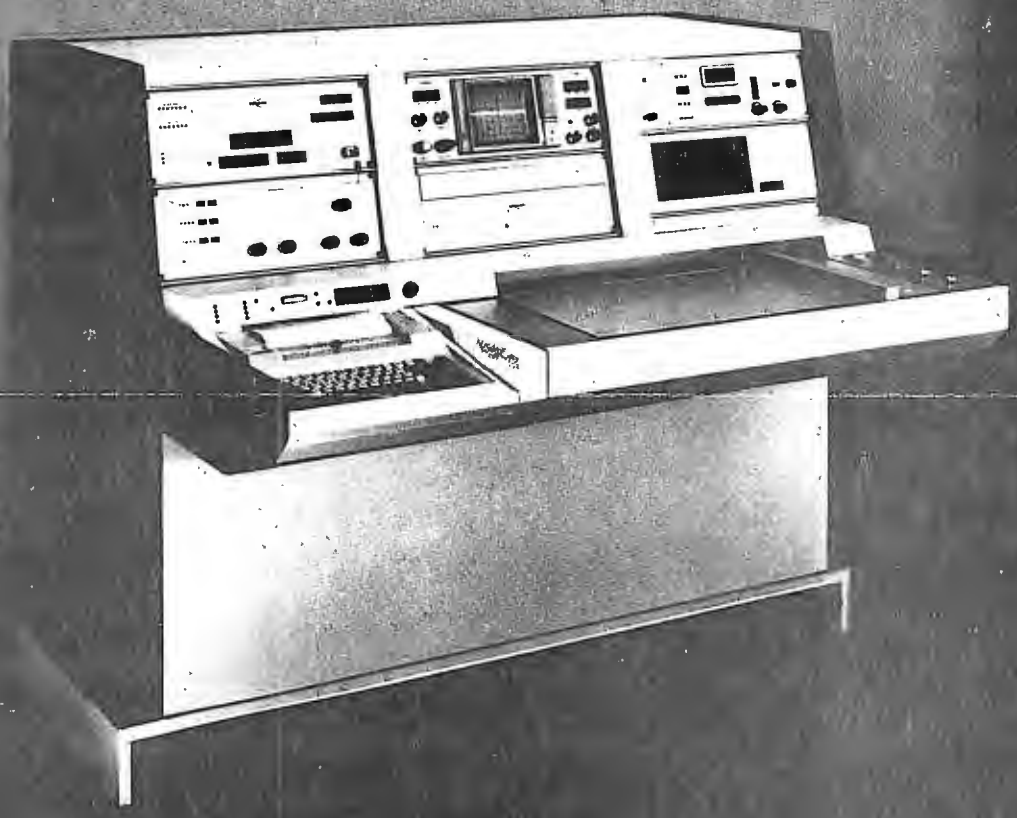
Yours sincerely

Horst

BRUKER

BRUKER announces a new landmark
in low-cost high-resolution
superconducting NMR spectrometers with

^{1}H frequency of 250 MHz



The University of Alabama in Birmingham
Comprehensive Cancer Center

January 10, 1979

Dr. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Postdoctoral Position

Dear Barry:

I have a postdoctoral opening in my laboratory at the Cancer Center. The candidate will work on an NIH funded project involving conformational studies of peptides using various NMR techniques including paramagnetic probes and multiple resonance methods. Prior experience in this area would be helpful. The facilities include Bruker HX-90, CXP-270 and WH-400 NMR spectrometers. Interested candidates may send a resume and arrange for three letters of recommendation to reach me at the Cancer Center. Another postdoctoral position involving similar work is available in the laboratory of my colleague, Dr. Jerry D. Glickson. Interested candidates may address enquiries to him directly. The University of Alabama in Birmingham is an equal opportunity affirmative action employer.

Yours sincerely,

Ramu

N.R. Krishna, Ph.D.

NRK/tc

cc

STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305

STANFORD MAGNETIC RESONANCE LABORATORY

(415) 497-4062
(415) 497-6153

January 11, 1979

Professor B. L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

RE: FT-NMR Spectra of Homo-Oligomethionine Peptides in the Helix-Supporting Solvent; Trifluoroethanol.

Dear Professor Shapiro:

As part of a continued collaboration with Professor Murray Goodman (UC San Diego) and Fred Naider (City University of New York), I have recently focused on obtaining ^1H NMR spectra of dilute peptides in the helix-supporting solvents, trifluoroethanol (TFE) and trimethylphosphate (TMP). CD studies show that γ-ethyl-L-glutamate oligopeptides begin forming helices at a critical size--the heptamer--in these solvents (1). Similarly, L-methionine oligopeptides form helices at the heptamer in TFE (2,3), and L-alanine oligopeptides form helices between the hexamer and heptamer in TFE/1% H_2SO_4 (4).

By high resolution ^1H NMR one might describe the oligopeptide structures both above and below the critical size in a more detailed manner than is possible by inspection of CD spectra. TFE and TMP, however, present two strong solvent lines which dominate the ^1H NMR spectra (Fig. 1A). The usual recourse to obtain peptide spectra in these solvents hence has been the use of correlation methods sweeping over the amide region downfield of the solvent lines (5). It is known, however, that a solvent line can be selectively removed from a spectrum by preirradiation with a long single frequency burst of rf power (6). This finds its usual application in the elimination of the "water peak" in the high resolution spectrum of a biochemical solute (7). We thus undertook a mere extension of the saturation technique from the case of one solvent line (water) to two solvent lines (TFE or TMP). Two of the three decouplers available on the modified HXS-360 instrument at Stanford were used simultaneously to reduce the intensity of both solvent lines. We have found this procedure to work quite well and have recorded ^1H NMR spectra for linear oligopeptides of L-methionine at mM concentrations in TFE.

Professor B. L. Shapiro
January 11, 1979

As seen in Fig. 1B, the two-solvent peak irradiation technique gives the usual advantages of FT over correlation techniques, i.e., simultaneous observation of the aromatic, amide and aliphatic regions and the convenient use of TMS as a direct internal reference. Fig. 1C shows the NH region of the methionine heptamer in the helical conformation in TFE. Several NH resonances are resolved while two NH peaks at ~7.8 ppm overlap. We hope to obtain the NMR assignments of these NH resonances using specifically deuterated methionine peptides.

Please credit this contribution to Professor Oleg Jardetzky's subscription.

Sincerely,

Anthony Ribeiro

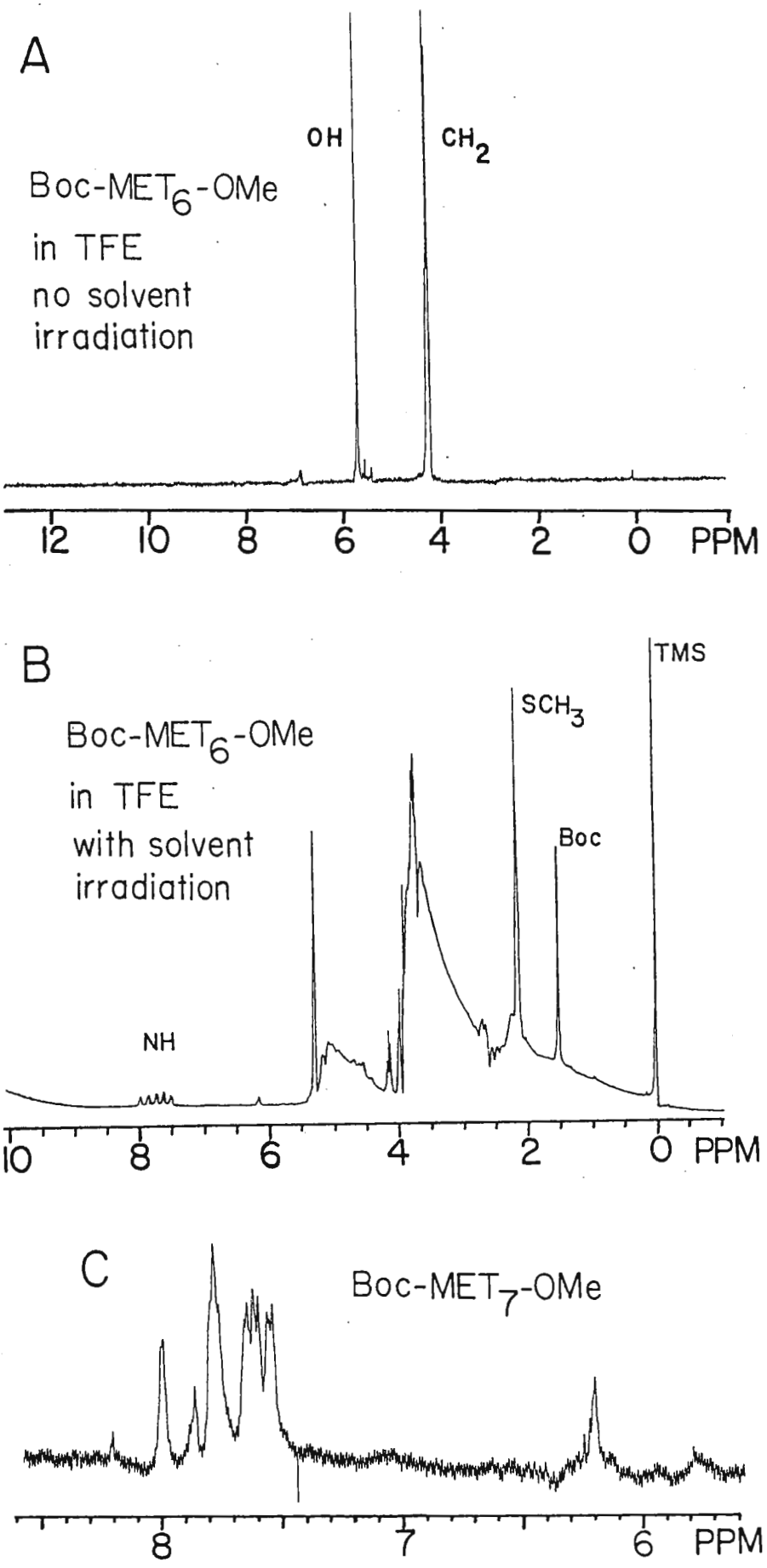
Anthony Ribeiro

AR/aw

REFERENCES:

1. M. Goodman, A. S. Verdini, C. Toniolo, W. D. Phillips, and F. A. Bovey, Proc. Nat. Acad. Sci. USA 64, 444-450 (1969).
2. J. Becker and F. Naider, Biopolymers 13, 1747-1750 (1974).
3. G. M. Bonora and C. Toniolo, Biopolymers 13, 2179-2190 (1974).
4. M. Goodman, F. Naider and R. Rupp, Bioorg. Chem. 1, 310-328 (1971).
5. T. P. Pitner, J. D. Glickson, R. Rowan, J. Dadok and A. A. Bothner-By, J. Amer. Chem. Soc. 97, 5917-5918 (1975).
6. J. Schaefer, J. Magn. Res. 6, 670-671 (1972).
7. D. I. Hoult, J. Magn. Res. 21, 337-347 (1976).

FIGURE 1


A
OH
CH2
Boc-MET6-OMe
in TFE
no solvent
irradiation
12
10
8
6
4
2
0
PPM
B
TMS
SCH3
Boc-MET6-OMe
in TFE
with solvent
irradiation
Boc
NH
10
8
6
4
2
0
PPM
C
Boc-MET7-OMe
8
7
6
PPM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014

NATIONAL HEART, LUNG, AND BLOOD INSTITUTE

January 15, 1979

Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

NIH/EPA Chemical Information System: New Search Capabilities in the Carbon-13 NMR Data Base

Dear Dr. Shapiro,

Recently, some major changes and additions have been made to the NIH-EPA Chemical Information System (CIS). One such change that may be of interest to readers of the NMR NEWSLETTER concerns the Carbon-13 NMR Search System (CNMR).

The CNMR data base has been doubled in size and now contains over 8,000 spectra. Each compound is identified by CAS Registry Number and, where possible, the spectral lines are all assigned. The file can be searched by shift or by full spectrum and also by Registry Number or full or partial molecular formula.

A more interesting way of searching the file is by substructure. This can be done in the CIS Component known as SANSS - for Structure and Nomenclature Search System. Within SANSS, one can search through the CNMR data base for all compounds that contain a particular sub-structure, such as an O-methyl group and retrieve the mean value of the shift for that type of carbon.

This program has been in use for over six months at NIH and we are finding it to be very useful. Its major deficiency is that there are misassigned spectra in the data base, but the search does in fact serve to isolate these and is being used by the CIS staff as a means of identifying and correcting errors in the data base.

Both SANSS and CNMR are available to all CIS subscribers. The CIS is run on a commercial system at Interactive Sciences Corporation (ISC) with an annual subscription fee of $300 per organization. Use of SANSS is priced at $60 per elapsed hour and CNMR costs $36 per hour. A full sub-structure search as described below will cost therefore between $5 and $20.

We will be pleased to supply anyone with a more complete description of this CNMR/SANSS search capability, an example of which is illustrated below. Interested readers may also refer to a forthcoming paper describing the search programs (1). Further information as to how to obtain access to the CIS may be obtained from Ms. Kay Pool of the ISC Washington Office, (202) 223-6503. If you have any comments or questions, please contact us at NIH.

Yours sincerely,

Cherie Fisk

G. A. Milne

Cherie L. Fisk
Lab. of Chemical Physics
NIAMDD
(301)496-1024

G. A. Milne
Lab. of Chemistry
NHLBI
(301)496-3341

(1) "Spectra-Structure Relationships in Carbon-13 Nuclear Magnetic Resonance Spectroscopy. Results From a Large Data Base." G.W.A. Milne, J. Zupan, S.R. Heller, and J. Miller, Org. Magn. Res., In Press, 1979.

Example of a CNMR substructure search.

In this example, the SANSS/CNMR link will be used to find the carbon-13 chemical shifts of the secondary acetylenic carbons in the structure, CH3-C###C-CH2------, where ### represents a triple bond. The following steps are followed: (1) The four-carbon chain may be built using the SANSS option CHAIN. (2) Single and triple bonds are then specified between appropriate carbons using the SBOND option. (3) This "query structure" (which may be displayed at any time using D) is then used in a FPROBE search which creates a temporary file of compounds containing this fragment. (4) A limit of acceptable branching in matched structures is imposed by the option TERMA, whereupon SUBNMR creates a file of matched substructures that is accessable by (5) going to the CNMR component. (6) Within the CNMR component, SUB shows the distribution of shifts specific to the atom of choice in the query structure; and (7) SPEC retrieves any spectrum by number.

The example is a representation of an actual dialog between user and CIS. The user's entries have been underlined and lengthy output, unnecessary for this illustration, deleted at points marked with ***.

```
    COMPONENT? *** SANSS
    ***
    COLLECTION SELECTED:   3

(1) OPTION? CHAIN 4

(2) OPTION? SBOND 1 2 3 4
    BOND TYPE (H FOR HELP) = CS

    OPTION? SBOND 2 3
    BOND TYPE (H FOR HELP) = CT

    OPTION? D
    1**2##3**4

(3) OPTION? FPROBE
    ***
    FRAGMENT:
              3C#####2C*****1C

    REQUIRED OCCURRENCES FOR HIT :  2
    THIS FRAGMENT OCCURS IN    47 COMPOUNDS
    FILE =  1,    47 COMPOUNDS CONTAIN THIS FRAGMENT

(4) OPTION? TERMA 1 1 4 2
    THE FOLLOWING LIMITING CONNECTIVITY NODES
                        HAVE BEEN SPECIFIED:
      NODE   MAX NEIGHBORS
        1           1
        4           2
    OPTION? SUBNMR 1
    DOING SUB-STRUCTURE SEARCH
    ***
    FILE = 2   SUCCESSFUL SUB STRUCTURES =    7


(5) OPTION? GO CNMR
    NIH:EPA:NIC CARBON-13 NUCLEAR MAGNETIC RESONANCE
    SPECTRAL SEARCH SYSTEM -  Version 4.4
    ***
(6) Option? SUB
    Substructure Atom Number: 2
       8 spectra with specified atom;
       7 Assigned and    1 Unassigned.
    For    7 shifts:
    Average =  75.6 +/-  1.9 ppm
    Range   =  72.6 to  78.9 ppm
```

```
Type A(ssigned),U(nassigned),H(istogram), or E(xit):A
   ID# 1286  REGN:        503173      72.6 ppm
   ID# 1165  REGN:        629492      75.3 ppm
   ID#   60  REGN:        764012      78.9 ppm
   ID# 1148  REGN:        764352      74.9 ppm
   ID# 1150  REGN:       1119659      75.4 ppm
   ID# 3358  REGN:       1119659      77.0 ppm
   ID# 1153  REGN:       2809678      75.2 ppm
Type A(ssigned),U(nassigned),H(istogram), or E(xit):H
Histogram resolution (ppm): 1
                ==========================
  70 ppm  n=  0 :
  71 ppm  n=  0 :
  72 ppm  n=  1 :*
  73 ppm  n=  0 :
  74 ppm  n=  1 :*
  75 ppm  n=  3 :***
  76 ppm  n=  0 :
  77 ppm  n=  1 :*
  78 ppm  n=  1 :*
  79 ppm  n=  0 :
  80 ppm  n=  0 :
  81 ppm  n=  0 :
                ==========================
Type A(ssigned),U(nassigned),H(istogram), or E(xit):U
   ID# 8689  REGN:     28467756

Type A(ssigned),U(nassigned),H(istogram), or E(xit):E

(7) Option? SPEC
    ID #: 60

    O**C3*C1#C2*C4
        2-Butyn-1-ol
    WLN: V2UU2
    REGN =       764012      CMR#    60      MW =  70.04
    C4 H6 O1
    L.F.JOHNSON,W.C.JANKOWSKI,C-13NMRSPECTRA,
                        JOHNWILEY&SONS,NY,(1972).
    Solvent:    DIOXANE
     SHIFT   MULT   INTENS   ASSIGN
      80.0     S       43       1
      78.9     S       47       2
      50.5     T       99       3
       3.2     Q       67       4
```

WAYNE STATE UNIVERSITY
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DEPARTMENT OF CHEMISTRY

January 15, 1979

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
Title: CMR Study of Alkali Metal Chelation by 3-Alkylpentane-2,4-dionates.
Postdoctoral position available.

Dear Dr. Shapiro,

We have found that CMR spectroscopy is a useful tool for studying alkali metal chelation by enolate anions of β-diketones. We have examined the low temperature CMR spectra of sodium salts of pentane-2,4-dione (1), 3-methylpentane-2,4-dione (2), and 3-ethyl-pentane-2,4-dione (3) and the effect of added lithium ion on the spectra. The spectra reflect the presence of chelated (Z,Z) and dissociated species (E,Z) which differ in configuration at C-C partial double bonds and which, at low temperatures, interconvert slowly on the NMR time scale.

The sodium salt of 1 (0.4 M in methanol) exists as a mixture of the two forms shown in equation 1. While the 3-alkyl derivatives exist solely as the dissociated E,Z form. While the enolates from (2) and (3) do not appreciably chelate sodium at these concentrations they can be converted to about 70% of the chelated structure by addition of lithium ion (1 mole) which is more strongly chelated (eq 2 and 3).

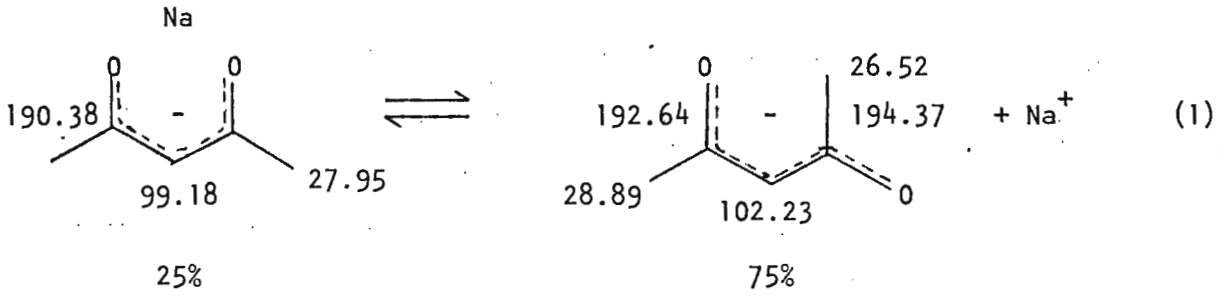
A full paper detailing this work has been prepared and preprints are available on request.

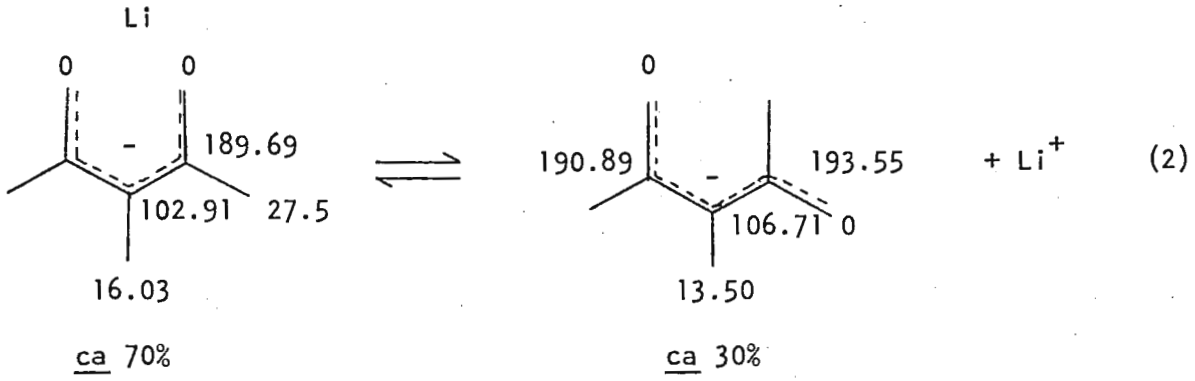
We will have an opening for a post-doctoral research associate ($11,000 pa) to begin soon. Interested parties are encouraged to write to me. They should send a copy of their resume and should arrange for two or three letters of recommendation. We are currently expanding our capabilities with the acquisition of a new high field spectrometer (Nicolet, 300 MHz).

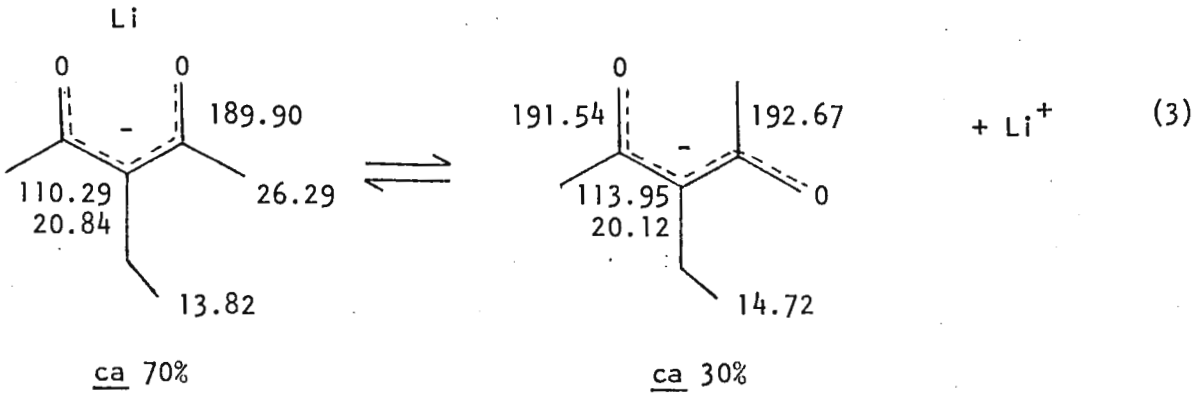
Sincerely yours,

Morton Raban
Professor of Chemistry

MR:bl


Na
190.38
99.18
27.95
192.64
28.89
102.23
26.52
194.37
+ Na+
(1)
25%
75%


Li
189.69
102.91
27.5
16.03
190.89
106.71
193.55
13.50
+ Li+
(2)
ca 70%
ca 30%


Li
189.90
110.29
20.84
26.29
13.82
191.54
113.95
20.12
192.67
14.72
+ Li+
(3)
ca 70%
ca 30%

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CENTRAL RESEARCH & DEVELOPMENT DEPARTMENT
EXPERIMENTAL STATION

January 16, 1979

Dr. Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, TX77843

Dear Barry,

Resonance Shifts in Multi-Channel Decoupling Experiments

While studying the $^{13}C_{^{19}F}$ spectra of fluorinated compounds using multi-channel high power ^{19}F decoupling (1) we encountered large Bloch-Siegert shifts (2,3). We have investigated these further using a Varian XL-100 set to observe fluorine at 94.1 MHz in the CW mode. Fluorodibromomethane ($CHFBR_2$) was studied with fluorotrichloromethane as lock. The ^1H resonance of $CHFBr_2$ was located using weak CW irradiation at 100 MHz from the 'gyrocode' decoupler to collapse the ^{19}F doublet (J = 50 Hz). A second ^1H irradiation source was provided by an H_p 230 rf amplifier driven by a General Radio 1061 synthesizer. The two rf sources were combined in an ENI PM12-2 power combiner and fed to the probe. With the H_p 230B off, the 'gyrocode' frequency was set to irradiate the $CHFBr_2$ protons and its power level raised to just collapse the ^{19}F doublet. Using the INDOR mode, the center of the ^{19}F doublet was monitored as the gyrocode was swept through the proton resonance. When the second rf source was switched on, the Bloch-Siegert shift experienced by the protons was indicated by the shift in the 'INDOR' peak. A series of spectra obtained with the second rf source set to a given rf power level and at a number of different offsets from the proton resonance is shown in the figure. Ramsey (3) derived the following expression for generalized Bloch-Siegert shifts:

$$\nu = \nu_o + (\gamma H_2)^2/2(\nu_o - \nu_2)$$

where ν is the perturbed resonance frequency, ν_o is the resonance frequency in the absence of a perturbing field, γH_2 is the magnitude of the perturbing field and ν_2 its frequency. Shifts measured from the figure were used to calculate values for γH_2 via Ramsey's equation. The Table shows that this equation is obeyed quite well.

Sincerely,

Derick W. Ovenall

Derick W. Ovenall

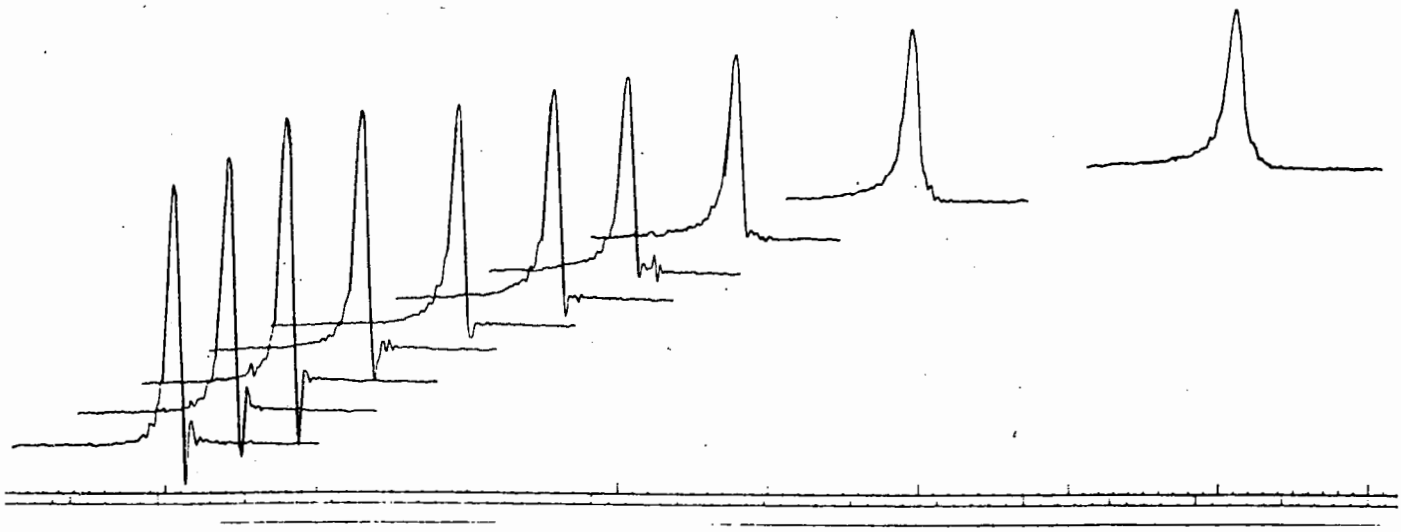
James J. Chang

James J. Chang

References

1. D. W. Ovenall and J. J. Chang, Newsletter No. 212, J. Mag. Res. 25, 361 (1977).
2. F. Bloch and A. Siegert, Phys. Rev., 57, 522 (1940).
3. N. F. Ramsey, Phys. Rev., 100, 1191 (1955).

INDOR sweep display of ^{19}F nmr spectra of $CHFBr_2$ as a function of offset of the second decoupler. From left to right the offset of the second decoupler for each trace is: off, 20, 10, 6, 4, 3, 2.5, 2.0 1.5, 1.0 KHz.



Resonance Shifts as Function of Offset of Second Decoupler

Offset	Resonance Shift	(γH_2) in Hz
20000 Hz	9.4 Hz	613
10000	19.0	616
9000	21.5	622
8000	24.1	621
7000	27.6	622
6000	31.9	619
5000	38.6	621
4000	48.2	621
3000	64.1	620
2000	94.9	616
1000	179.0	598

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Afdeling

Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
USA

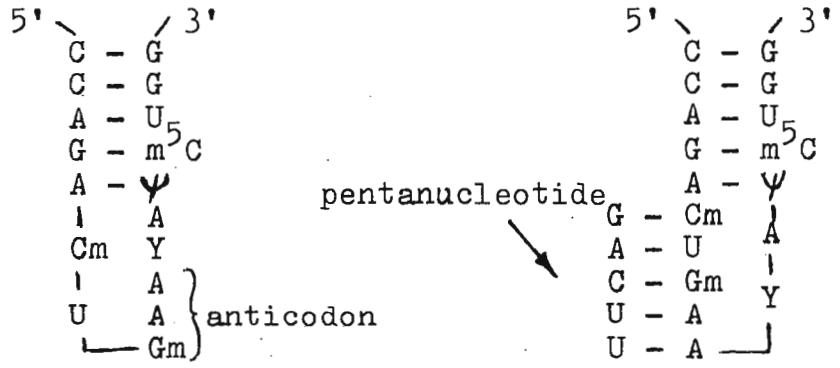
Uw kenmerk | Uw brief van | Ons kenmerk

Datum January 16, 1979

Onderwerp Codon-anticodon interaction in tRNA.

Dear Professor Shapiro,

Transfer RNA's (tRNA's, molecular weight about 30.000) play a fundamental role in decoding the genetic message on the messenger RNA into the defined amino acid sequence of proteins. tRNA's contain a triplet base sequence - the anticodon - which during protein synthesis recognizes a complementary triplet base sequence on the messenger RNA - the codon - which codes for a particular amino acid. At present we are using NMR to study how binding of the codon-triplet affects the structure of tRNA. We are mainly working with $tRNA^{Phe}$ isolated from yeast using different oligonucleotides all containing the codon UUC. Particularly interesting results were obtained with the pentanucleotide UUCAG which is complementary to the five bases at the 5' side of the anticodon loop of yeast $tRNA^{Phe}$.



Anticodon branch with anticodon loop in 3' stack as in the X-ray structure model of yeast $tRNA^{Phe}$.

anticodon branch with anticodon loop in 5' stack as found by NMR.

At low temperature (1°C) the hydrogen bonded imino protons of the pentanucleotide tRNA complex can be observed by NMR as is illustrated in Fig. 1. Fig. 1A represents the hydrogen bonded imino proton spectrum of the tRNA before and Fig. 1B after addition of UUCAG.

The difference spectrum B-A gives the resonances of the imino protons hydrogen bonded between the tRNA and UUCAG (indicated by sticks). It is concluded from this experiment that the pentanucleotide forms a complex with five basepairs. This is a very interesting result since such an extensive basepairing is not possible in the tRNA structure derived from X-ray diffraction studies which only permits the formation of three basepairs. In the X-ray model the bases of the anticodon loop are arranged in a socalled 3' stack (see scheme above). From the resonance positions of the hydrogen bonded protons of the pentanucleotide tRNA complex it follows that most likely a normal RNA double helix is formed with five bases on the 5' side of the anticodon loop stacked upon each other.

Sincerely yours,

H.A.M. Geerdes J.H. van Boom C.W. Hilbers
(State University)
Leiden

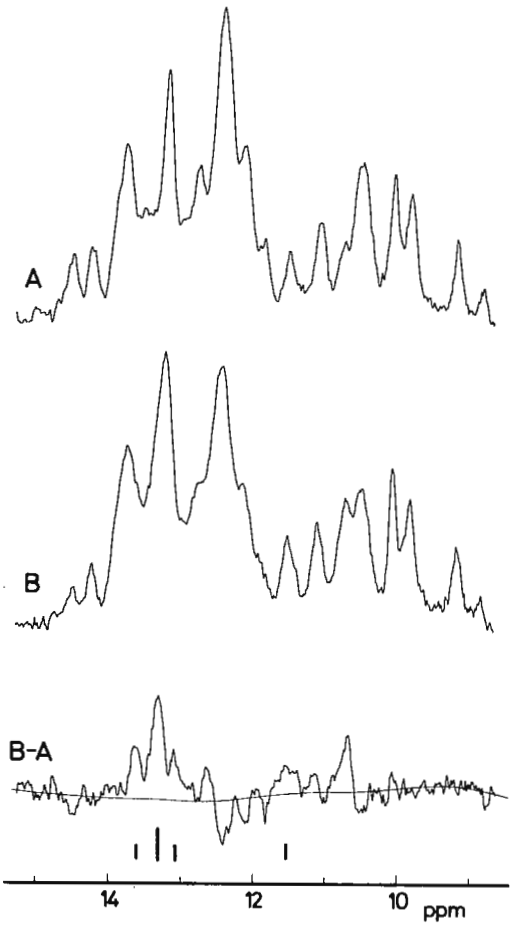


Fig. 1.
360 MHz NMR spectra of the hydrogen bonded protons in yeast $tRNA^{Phe}$ (1 mM) before (A) and after (B) addition of 3.8 mM UUCAG. Spectra were recorded at 1°C, in the absence of Mg^{2+} and at neutral pH. The difference spectrum at the bottom of the figure represent the spectra B minus A.

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GBF
Gesellschaft für
Biotechnologische
Forschung mbH

Abteilung

Physikalische Meßtechnik

Professor B.L. Shapiro,

Department of Chemistry,
Texas A & M University,
College Station,
Texas 77843,
USA.

Ihre Nachricht vom	Telefon 05 31/70 08-1	Telefondurchwahl	Datum
		05 31/70 08 362	16.1.79.

^{13}C chemical shifts of solvents and a general moan

Dear Dr. Shapiro,

For the ^{13}C n.m.r. user the chemical shifts of the carbon atoms of the deuterated solvents can be particularly important as these may be used as secondary references, although it must be remembered that the solute can affect these values. Reference to the commonly available textbooks, however, leaves one slightly confused in that the shift for a particular solvent can vary by up to 1 ppm. For consistency we have measured all the commonly encountered solvents as pure solvent with 10% by volume of TMS on our Varian CFT-20 at 34°C. These values, together with other useful physical data, are reported in the table.

Our recent experiences with attempts at data extraction of chemical shifts from the literature has prompted us to plead that all spectroscopists should take note of the IUPAC Recommendations on NMR Spectra (Pure Appl. Chem., 1976, 45, 219, see Becker's TAMU NMR Newsletter, 1977, 231, 2). We are sure that propagation of these recommendations by service departments to the public (synthetic organic and inorganic chemists) would greatly alleviate nervous breakdowns of reviewers. The main culprits seem to be those people reporting fluorine and phosphorus data. It is particularly important to state the reference and the sign convention.

Yours sincerely,

Victor Wray Ludger Ernst

Victor Wray Ludger Ernst

Table. ^{13}C chemical shifts[a] and physical properties of the important solvents.[b]

Solvent	Shift	d_4^{20}	m.p.	b.p.
d_6-Acetone	205.8(C-2), 29.8(C-1)	0.87	-95	56
d_3-Acetonitrile	118.1(C-1), 1.3(C-2)	0.84	-46	82
d_6-Benzene	128.0	0.95	6	80
d_1-Chloroform	77.0	1.50	-64	62
d_{12}-Cyclohexane	26.3	0.89	7	81
Deuterium oxide	-	1.11	4	101
d_6-Dimethyl sulphoxide	39.5	1.18	18	189
d_8-Dioxane	66.4	1.13	12	101
d_4-Methanol	49.0	0.89	-94	65
d_2-Methylene chloride	53.8	1.35	-95	40
d_5-Pyridine	149.8(C-2),135.6(C-4), 123.5(C-3)	1.05	-42	116
Carbon disulphide	192.2(int) 192.7(ext)	1.26	-112	46
Tetrachloromethane	96.0	1.59	-23	77
d_8-Tetrahydrofuran	67.3(C-1), 25.3(C-2)	0.99	-65	67
d_8-Toluene	137.4(C-1),128.9(C-2), 127.9(C-3),125.1(C-4), 20.4(CH_3)	0.94	-95	111
Trifluoroacetic acid[c]	164.4(C-1),116.5(C-2)	1.54	-15	72

a) Pure solvent with 10% by volume of TMS.

b) The density is of the deuterated solvent and the m.p. and b.p. (^{o}C) are of the hydrogen-containing solvent.

c) $^{2}J_{FC}$ =44 Hz, $^{1}J_{FC}$ =283 Hz.

Wiss.Rat Dr. F.H. Köhler
ANORGANISCH-CHEMISCHES INSTITUT
DER
TECHNISCHEN UNIVERSITÄT MÜNCHEN

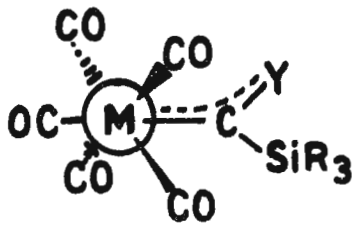
D-8046 GARCHING, den 17. 1. 79
Lichtenbergstraße 4
Ruf-Nr. (089) 3209/3080/3081 (Prof. Fischer)
3110 (Prof. Fritz)
3130 (Prof. Schmidbaur)
/3109

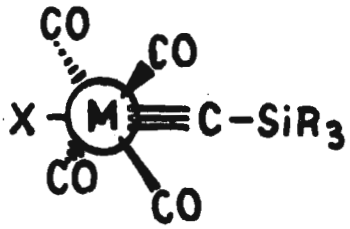
Prof. B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77 843

Title: $\delta(^{29}Si)$ and $J(^{183}W-^{29}Si)$ in organometallics

Dear Professor Shapiro!

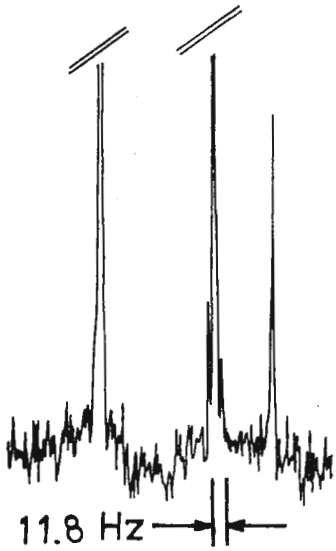
The preparative chemistry in this institute includes a good deal of silicon activities. We clearly needed a powerful ^{29}Si-probe to monitor this nucleus by FT nmr and decided to add a ^{29}Si-channel to our HX 90 instrument. Very often our compounds contain phosphorous and silicon at the same time. So we ordered a $^{29}Si\{^{1}H,^{31}P\}$ probe head. Until now however, the signal to noise is rather unsatisfactory when irradiating ^{1}H and ^{31}P simultanously. So the first series of metal carbene (I) and carbyne (II) complexes we investigated did not contain phosphorous.

I 

II 

M = Cr, Mo, W
Y = OR', NR'_2
R = Me, Ph
X = Cl, Br, J

Trends of $\delta(^{29}Si)$ show that metal carbene and carbyne fragments ($M=C\overset{Y}{<}$ and $M\equiv C-$) behave as α,β-unsaturated organic groups. We also find that the dependence of $\delta(^{29}Si)$ on the metals Cr, Mo and W reflects the lanthanide contraction. On the other hand $\delta(^{29}Si)$ ranges do not allow one to differenciate between carbene and carbyne complexes. But help could come from $J(^{183}W-^{29}Si)$ which do not seem to have been measured before. Even though we were limited by the thermal lability of I and II (spectra were run at -20 to -30°C) and S/N we obtained four representative examples, the first one is also shown in the figure. The signal of interest in the middle

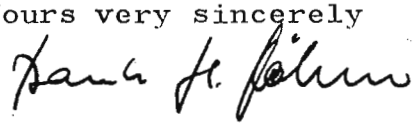


	$\delta(^{29}Si)$	$^{2}J(^{183}W-^{29}Si)$
$(CO)_5W=C\overset{OMe}{<}SiMe_2Ph$	- 1.5	11.8 Hz
$(CO)_5W=C\overset{OMe}{<}SiPh_3$	-18.3	12.5 Hz
$C_5H_5(CO)_2W\equiv C-SiMePh_3$	-20.7	55.9 Hz
$Br(CO)_4W\equiv C-SiPh_3$	-23.4	44.1 Hz

is accompanied by the standard ($Me_3SiOSiMe_3$, calculated relative TMS) and a small one due to a thermal decomposition product. Clearly, $^2J(^{183}W-^{29}Si)$ is bigger for carbynes than for carbenes, a fact which parallels our findings for $^nJ(^{183}W-^{13}C)$ [1, 2]. A detailed discussion of our results will appear in J. Organometal. Chem.

Please credit this letter to the subsciption of Prof. H.P. Fritz.

Yours very sincerely



1 F.H. Köhler, H.J. Kalder and E.O. Fischer, J.Organometal. Chem. 85(1975)C19.
2 F.H. Köhler, H.J. Kalder and E.O. Fischer, J.Organometal. Chem. 113(1976)235.

245-35

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January 25, 1979

Professor B. L. Shapiro
Chemistry Department
Texas A and M University
College Station, TX 77843

Six Million-to-One and Rising!

Dear Barry:

After a hectic nine months of post-introduction activities, we are now getting to the point of taking advantage of the enormous dynamic range capability of the XL-200. Proton nmr experiments in H_2O solution have always been difficult for many reasons: (a) the magnetization available, even in a 5 mm tube, is often so large that even with the 13-bit ADC in the XL-200, pulses less than 30° must be used if the unperturbed, completely relaxed spectrum without any magnetization transfer is to be obtained; (b) the preamps and IF amplifiers must be extremely linear to avoid or minimize harmonic distortion; (c) the noise must be adequately digitized for meaningful time-averaging; (d) the signals must not be allowed to be "clipped" in the ADC; (e) assuming (a)-(d) above have been satisfied, the time-averaging process requires computer word resolution consistent with extremely large time-domain signals. Since each pulse can generate a signal of 2^{11} (+ sign) using a 12-bit ADC, the number of total transients can be very limited before overflow would occur. For example, using a 16-bit computer word, 16 (2^4) transients would ideally fill the 15 bits available for signal ($2^{11} \times 2^4 = 2^{15}$). However, signals and noise are both present at all points in the FID. In the most carefully adjusted situations, only 1 bit of noise is digitized per transient. Since during time-averaging, noise grows with the square-root of the number of scans, the above 16 transients would automatically generate 2 bits of noise, producing a signal + noise of $2^{15} + 2^4 \approx 2^{15}$. Obviously, the noise obtained during time-averaging does not materially effect the maximum number of transients which can be obtained. After these 16 scans, however, time-averaging must be stopped. For a 20-bit word, 2^8 (256) transients may be averaged, and for a 24-bit computer word 2^{12} or 4096 transients are possible. Increasing the computer word size to 32 bits allows considerably more time-averaging of up to 2^{20} or 1048 K transients before time-averaging must be ceased. Use of a 13-bit ADC, although allowing up to a factor of two in real sensitivity in these ADC-limited situations, will correspondingly reduce the maximum number of transients permissible (although the same S/N ratio would be achieved in one-fourth the number of transients). Clearly, for meaningful long-term averaging at very low concentrations (< 10 ppm) a large computer word length is required.

Assuming that (a)-(e) are satisfied and that the time-averaged data are valid, the exponential weighting, Fourier transformation, and data presentation must not introduce significant errors. Integer mode exponential weighting and Fourier transformation do lose several bits of precision in round-off errors and will always degrade the final signal-to-noise ratio. The very size of the computer word restricts the max-

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imum number which can be handled. An x-bit computer word places an upper limit on any number 2^{x-1} (one bit for sign), thus effectively restricting the accuracy of any number to one part in 2^{x-1}. Round-off errors in an 8 K integer transform amount to ~ 2 bits of precision, for a 32 K integer transform, ~ 4 bits. Consequently, while the computer can still produce a transformed peak intensity of 2^{x-1}, the noise resulting from round-off errors alone in a 32 K transform is $\sim 2^4$, resulting in a real dynamic range of 2^{x-5} ($\sim$ 32,000 for a 20-bit word, 524,000 for a 24-bit word, and 134 M for a 32-bit word). These maximum dynamic ranges are valid for noise-free FID's, since the noise was only assumed to arise from round-off errors in the transform calculations. In (e) we saw that the noise amplitudes in the most favorable situations were $2^{2.5}$, 2^4, and $2^{6.5}$ for 20-, 24-, and 32-bit word sizes. These noise contributions, however, will not significantly further degrade the dynamic range, since the noise will add in an RMS fashion. That is $\sqrt{(2^5)^2 + (2^{2.5})^2} \approx 2^5$. As a further complication, the dynamic range in the frequency domain can be, and usually is, significantly higher than in the time-domain. Thus, time-averaging can produce an FID which is entirely valid yet upon transformation produces a spectral peak which cannot be displayed or plotted without very significant digital noise.

The XL-200 avoids these problems by employing a 32-bit word size in its Acquisition Processor for signal averaging, and floating-point arithmetic in the weighting and transformation steps, thus retaining the full precision of the data. Floating-point math is capable of characterizing numbers from 10^{-38} to 10^{+38} with the same precision (a floating point number is represented in a 32-bit word as a 23-bit mantissa and 8-bit exponent). Very large signals and very small signals are measured with equal precision--to about one part in 8 million.

The spectrum confirms the high dynamic range possible--in this case about 6,000,000:1 S/N ratio for the H_2O resonance in a mixture of H_2O, D_2O, acetonitrile, methanol, and t-butylalcohol. The percentages given are in proton %. The same FID was transformed using integer math and the resulting spectrum plotted at the top at a gain setting of 2×10^4. The disadvantage of the integer transform is obvious. The data were accumulated for $\sim$ 14 hours using $\sim 25^{\circ}$ pulses. H_2O S/N of $\sim$ 700,000:1 was obtained in an analogous 1000 transient (8 min) accumulation, and $\sim$ 20,000:1 for a single pulse.

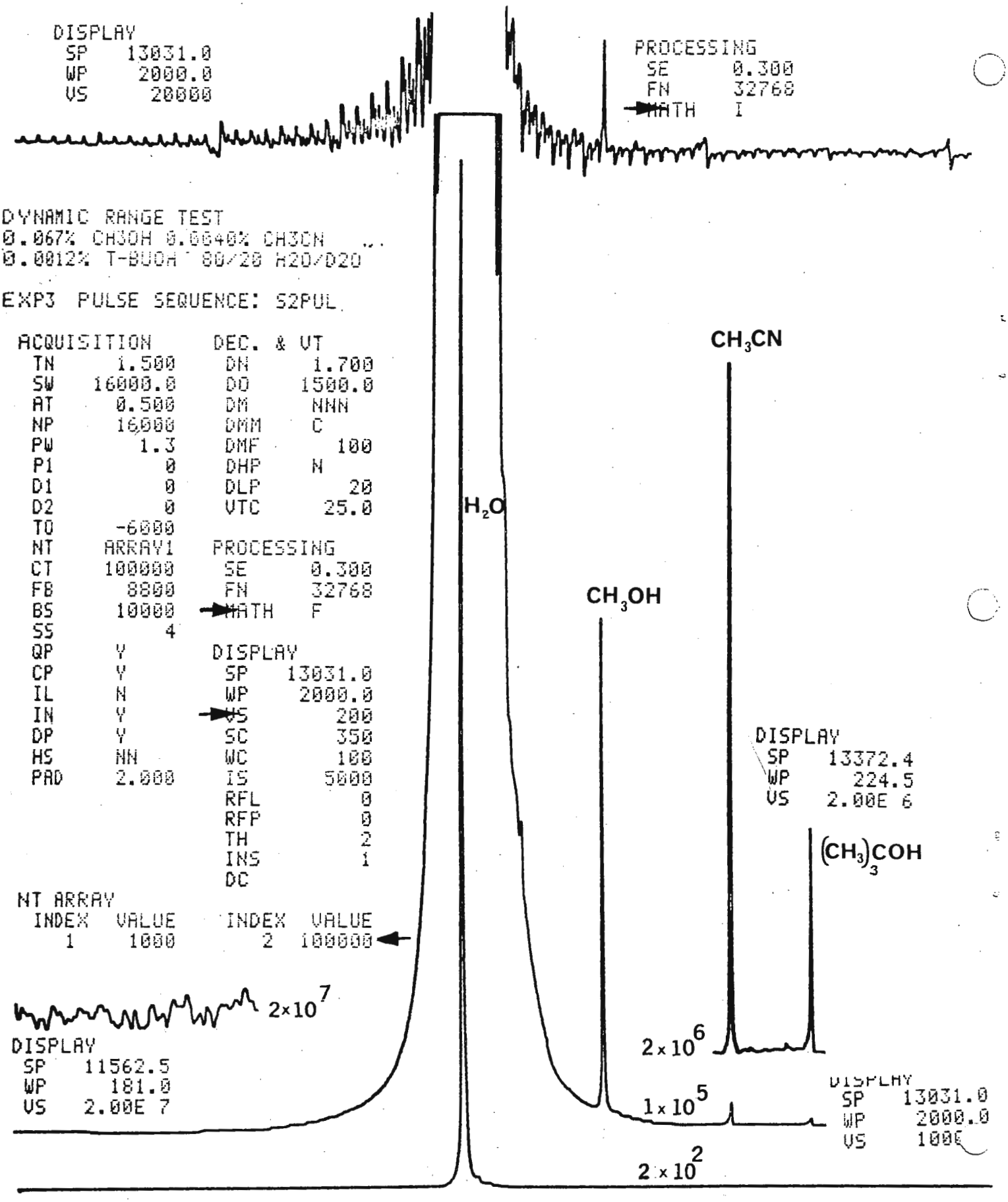
As far as S/N records go, only instrument time seems to be a problem!

See you at ENC,

George

George A. Gray, Manager
NMR Applications Laboratory
Varian Instrument Division

GG:cyt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MATH I
DYNAMIC RANGE TEST
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EXP3 PULSE SEQUENCE: S2PUL
ACQUISITION
TN 1.500
SW 16000.0
AT 0.500
NP 16000
PW 1.3
P1 0
D1 0
D2 0
TO -6000
NT ARRAY1
CT 100000
FB 8800
BS 10000
SS 4
QP Y
CP Y
IL N
IN Y
DP Y
HS NN
PAD 2.000
DEC. & VT
DN 1.700
DO 1500.0
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VS 1000
2x10^7
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1x10^5
2x10^2

A hot performer at a cool 4.2°K

Varian introduces: The XL-200 superconducting FT NMR spectrometer

In a cost- and resource-conscious world, the new XL-200 with 47-kG superconducting magnet makes a lot of sense. To begin with, its high-field performance and advanced design come in a truly affordable package. And economy characterizes the XL-200 spectrometer in other ways, too—such as the low-loss dewar unit, which lets the system operate over three months on only 25 liters of liquid helium!

The basic instrument is designed for ^{1}H (200 MHz) and ^{13}C (50.3 MHz) observation, but it will accommodate a host of other nuclei with the optional 20-80 MHz broadband accessory.

The XL-200's data management system tops all conventional concepts of versatility and convenience. There are two processing units working in tandem—one 32 bits wide and very fast for data acquisition, the other programmed in a high-level language and extremely flexible for data manipulation. Both operate continuously and, together with the XL-200's full complement of built-in I/O devices, offer you unique multi-tasking capability and high sample throughput.

And that's only the beginning of a long list of features which could read like your own NMR wishlist:

- 47-kG Nb-Ti superconducting magnet with 50-mm bore
- 25 liters liquid He dewar capacity; 3-month refill interval
- 35 liters liquid N_2 dewar capacity; 14-day refill interval (45 days with optional refrigerator)
- 5- and 10-mm samples standard; other sample sizes optional
- Broadband probes covering 20-80 MHz and 188-212 MHz ranges
- Flexible mix/match RF system with fixed-frequency sources such as ^{1}H, ^{13}C, ^{19}F, and ^{31}P
- Compatible with RF synthesizer for broadband multi-nuclear operation
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- Programmable 32K CPU for data processing and multi-tasking
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If you would like the balance of the features to compare with your wishlist, write Varian Associates, Inc., Box D-070, 611 Hansen Way, Palo Alto, CA 94303.

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V/RÉF.

N/RÉF. GJB/cc

Professeur B.L. SHAPIRO
Department of Chemistry
Texas A & M University
College of Science
College Station Texas
77843 USA

Genève, le 17 janvier 1979

Cher Professeur Shapiro,

Merci de votre lettre de rappel du 2 janvier 1979.

Notre groupe a continué de s'intéresser à l'emploi du magnétisme nucléaire dans le champ magnétique terrestre en vue du diagnostic médical. L'effort maximum a porté sur l'identification in situ de fluides physiologiques chez l'homme et sur la comparaison des temps de relaxation entre fluides physiologiques sains et les mêmes fluides physio-pathologiques.

Publications récentes : (ou en cours d'impression)
(on peut obtenir tirés à part ou preprints)

1) "Possibilités d'identification de diverses variétés de liquide amniotique par magnétographie nucléaire"

G. BENE, B. BORCARD, E. HILTBRAND, R. SECHEHAYE, P. MAGNIN et M. DUMONT, J.M. THOULON, D. RAUDRANT et B. BENE

Société Française de Médecine Périnatale
Septièmes Journées Nationales
Aix Les Bains 1977

Librairie Arnette, 2, rue Casimir-Delanque, Paris 1978

2) "Nuclear Magnetism of some physiological fluids in low fields"

G.J. BENE, B. BORCARD, E. HILTBRAND, P. MAGNIN
Ecole de Physique, DPMC, 1211 - Genève 4 - Switzerland

Résumé

Magnetic resonance applied to blood will probably lead to a non invasive method for early diagnosis of hyperviscosity. The method consists in measuring the relaxation time T_2 in a weak magnetic field (1) of the water

protons contained in blood. The physiological liquids are essentially solutions of ions and proteins. The magnitude of T_2 in the earth field H_T for the protons in the solvant water is particularly sensitive to the longest correlation times τ_c encountered in the solution. We have investigated the relaxation time T_2 of the blood "in vitro" and "in situ" as well as T_1 and T_2 for solutions of proteins such as albumin, α and γ globulins and hemoglobin.

20th Ampere Congress - Tallinn USSR (August 1978)
to be published.

3) "Magnetisme nucléaire - Identification de fluides physiologiques humains, in situ, par relaxation protonique dans le champ terrestre"

B. BORCARD, E. HILTBRAND, P. MAGNIN et G.J. BENE

Comptes Rendus de l'Académie des Sciences - Paris.

La possibilité de déterminer avec précision, in situ, le temps de relaxation spin-spin des protons, en champ faible, de fluides physiologiques et de liquides ingérés, ouvre la possibilité d'une technique nouvelle de diagnostic médical et vétérinaire.

The precise determination, in situ, of the proton spin-spin relaxation time in a weak field, of physiological or drunk fluids, opens a new medical and veterinary diagnosis method.

Deux mises au point d'ensemble sont actuellement en cours de publication.

1) "Medical diagnosis by nuclear magnetism in the earth field range"

G.J. BENE, B. BORCARD, E. HILTBRAND and P. MAGNIN

Chapter in the book "NMR in Medicine" in series "NMR Principles and Progress" - Springer Verlag

2) "Foundations and preliminary results on medical diagnosis by nuclear magnetism"

G.J. BENE

Chapter in vol. 49 (1979) of the series "Advances in electronics and electron physics" - Academic Press (New York)

Prochains meetings du Groupement Ampère :

a) IVth Specialized Colloque Ampère

Leipzig DDR
17 - 21 September 1979

"Dynamic Processes in Molecular Systems as studied by RF-spectroscopy"

Adresse pour information : Prof. Dr. A. Lösche
Physikalisches Institut der Karl-Marx Universität
Linnéstrasse 5
701 - LEIPZIG C1 - DDR

b) Joint ISMAR - Ampère Int. Conf. on Magnetic Resonance

XXI Ampere Congress

Delft (Netherlands)
25 - 30 August 1980

c/o K.l.v.l., 23 Prinsessegracht. The Hague

Adresse pour information : Prof. J. Smidt
Lab. voor Technische Natuurkunde
Lorentzweg - 1 DELFT
The Netherlands

Avec mes sentiments très cordiaux.

Prof. G.-J. Béné

Signé en son absence
par Mlle C. Chauffat
Secrétaire

245-43

LILLY RESEARCH LABORATORIES

DIVISION OF ELI LILLY AND COMPANY · INDIANAPOLIS, INDIANA 46206 · TELEPHONE (317) 636-2211

January 17, 1979

Professor B. L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dear Professor Shapiro:

Polyether Ionophores

Studies of the physical and chemical properties of the polyether ionophores have kept many nmr spectroscopists busy over the recent years. Perhaps some of these folks could use some tricks we have developed in dealing with these compounds.

The ionophores are obtained from the fermentations in the form of "mixed salts." These are primarily mixtures of sodium and potassium complexes, and their spectra are very discouraging. We have found that by shaking the deuterochloroform solution of this mixture with saturated brine, one can easily convert it to pure sodium salt. Analogous procedures may be used to easily generate the potassium and silver complexes; ions bound more weakly (e.g., Li^+ or Cs^+) may require several exposures to a saturated aqueous salt solution. All of this is easily done in the nmr tube, and we have used this technique to obtain ^1H nmr spectra of several salts of monensin.

It is also frequently desirable to convert the salts to the "free acid" form. This must be done with some care, due to the acid lability of these polyethers. We have found that shaking a chloroform or methylene chloride solution of the salt with aqueous dichloroacetic acid (chosen because its pK_a closely approximates those of the ionophores) leads to the generation of the pure free acid. We generally use a twofold excess of dichloroacetic acid, and we usually do this in a separatory funnel to minimize exposure of the polyether to acid. The procedure works even for "tender" ionophores such as K-41 (≡ A32887), which decompose under other conditions.

These tricks, taken in conjunction with some techniques of methylations, etc., developed by John Occolowitz, have allowed us to complete the structures of a number of minor factors of these polyethers. These results will be published in due course.

Sincerely,

LILLY RESEARCH LABORATORIES

Doug Dorma — Jon Paschal — Mary Ann Bogan

Douglas E. Dorman, Ph.D.
Jonathan W. Paschal
Mary Ann Bogan
Physical Chemistry Research
DED/JWP/MAB:vr

RIJKSUNIVERSITEIT GENT
LABORATORIUM
voor
ORGANISCHE CHEMIE

B-9000 GENT, January 17, 1979
KRIJGSLAAN 271 · S 4 Tel. 22 57 15
(België-Europa)

Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station TX 77843

Dear Dr. Shapiro,

ASSIGNMENT OF GEMINAL AND VICINAL ^{13}C-^{1}H COUPLING CONSTANTS BY "PSEUDO"-INDOR FT TECHNIQUE.

Difference selective population transfer (DSPT) proton-coupled carbon-13 spectra are obtained by subtracting an FID(π) with a selective π-pulse perturbation on a specific transition in the ^{13}C satellite ^{1}H-nmr spectrum, from an unperturbed FID(0).[1-4]
The technique is an FT-substitute for CW-INDOR and is praised for its high sensitivity and ease of accumulation.

Since some time we are using this technique for the assignment and sign determination of geminal and vicinal ^{13}C-^{1}H coupling constants of derivatives of cyclic amino acids.
From the practical point of view the realisation of DSPI-$\{^{1}H\}^{13}C$ spectra with a selective "soft" π-pulse ($\gamma H_2 \approx$ line width of the ^{13}C-satellite proton line) has some disadvantages.

1. It is necessary to know the correct frequencies of the ^{13}C satellite lines in the proton spectrum. Since direct observation of the latter is cumbersome (if possible at all) one needs the assignments of ^{2}J and $^{3}J(^{13}C$-$^{1}H)$ à priori.
2. The signal to noise ratio of the response is very sensitive to small drifts of the satellite frequencies, e.g. due to temperature or concentration changes during the time of the measurement.
3. Each "INDOR" spectrum contains information for only one carbon. The large number of satellites, even in relatively simple molecules damps down the enthusiasm and patience of the chemist.
4. The relatively long duration of the selective π-pulse (typically >1 second) allows transfer of population by relaxation processes, which results in "improper" response.

The better strategy that eliminates these disadvantages and allows time saving and routine assignment of ^{2}J and ^{3}J (C,H) couplings, is the use of a "hard" but less selective π-pulse ($\gamma H_2 \approx 4$ Hz), with the frequency ca. 3 to 4 Hz offset from a proton line of the ^{12}C isotopomers. All ^{13}C satellites (due to ^{2}J and ^{3}J) of that proton are now perturbed and the INDOR responses for all carbons coupling with the given proton are obtained in one experiment. There is a small loss of sensitivity (each satellite does not experience a π-pulse anymore), but the pulse is short, and secondary population transfer is completely absent. In order to assign all ^{2}J and ^{3}J ^{13}C-^{1}H couplings in a molecule it is sufficient to perform only one (such) INDOR experiment for each chemically non-equivalent group of protons. The following example of the N-methyl-hydantoin of thiazolidine carboxylic acid illustrates the potential of this method.

Figure 1.

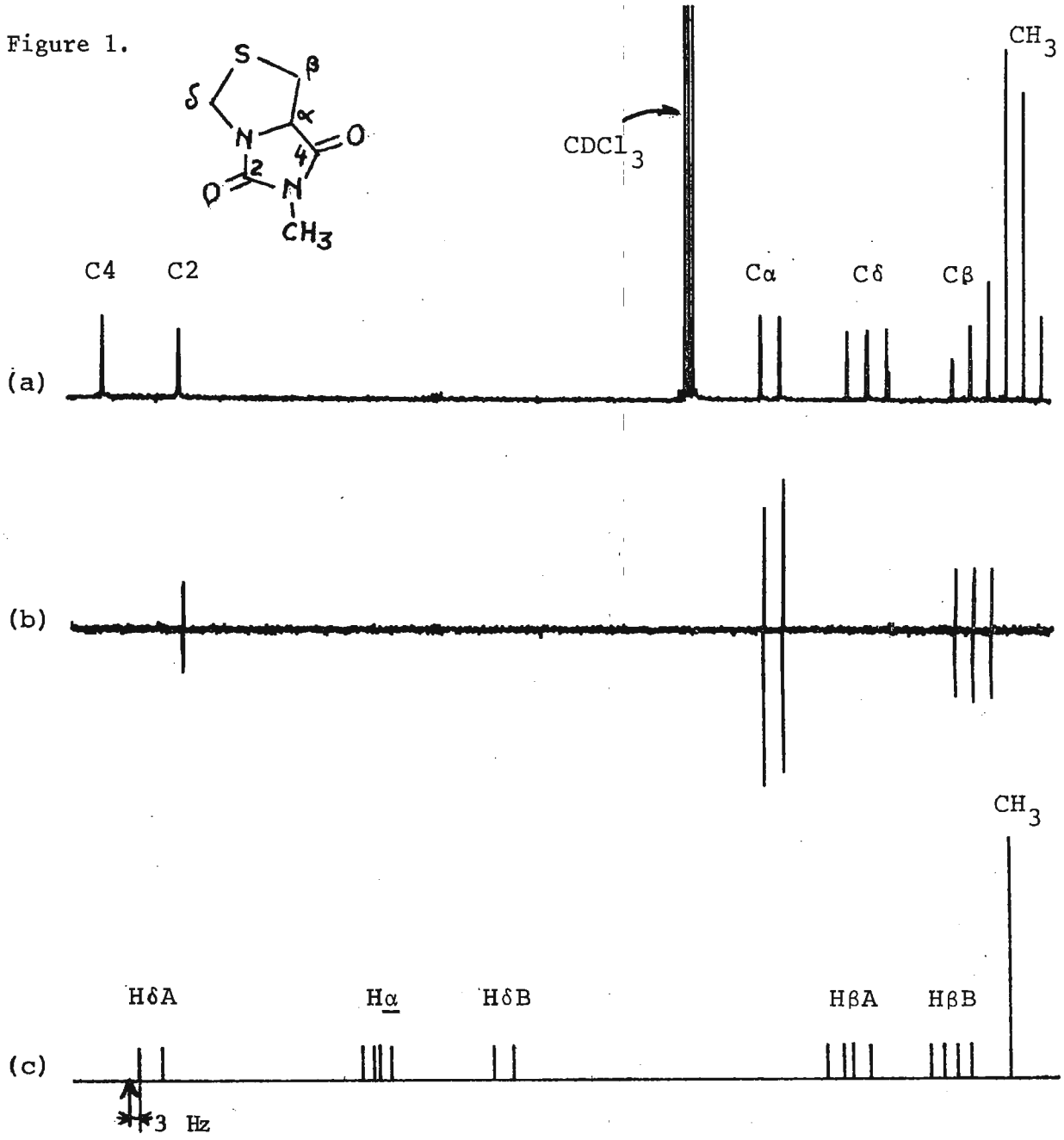

Fig. 1 shows (a) the proton coupled ^{13}C spectrum of the N-methylhydantoin of thiazolidine carboxylic acid; (b) the pseudo-INDOR spectrum obtained applying a π-pulse with ν_{H_2} = 4 Hz and τ = 0.125 sec (absolute intensity scale relative to (a)); (c) a schematic representation of the ^1H spectrum indicating the frequency of the π-pulse.

The individual INDOR responses on C2, Cα and Cβ are expanded in Figure 2a, b and c. This one INDOR spectrum gives the following information: $^3J(C2,H\delta A)$ = 3.9 Hz; $^3J(C\alpha,H\delta A)$ = 6.0 Hz; $^3J(C\beta,H\delta A)$ = 4.0 Hz; $^3J(C2,H\delta B)$ = 5.0 Hz; $^3J(C\alpha,H\beta A)$ = $^3J(C\alpha,H\beta B)$ = 2.5 Hz; $^3J(C\alpha,H\delta B) \simeq 0$ Hz; $^3J(C\beta,H\delta B)$ = 1.0 Hz; $^2J(C\beta,H\alpha)$ = 2.0 Hz; $^2J(H\delta A,H\delta B)/^3J(C2,H\delta B) < 0$; $^2J(H\delta A,H\delta B)/^3J(C\beta,H\delta B) < 0$.

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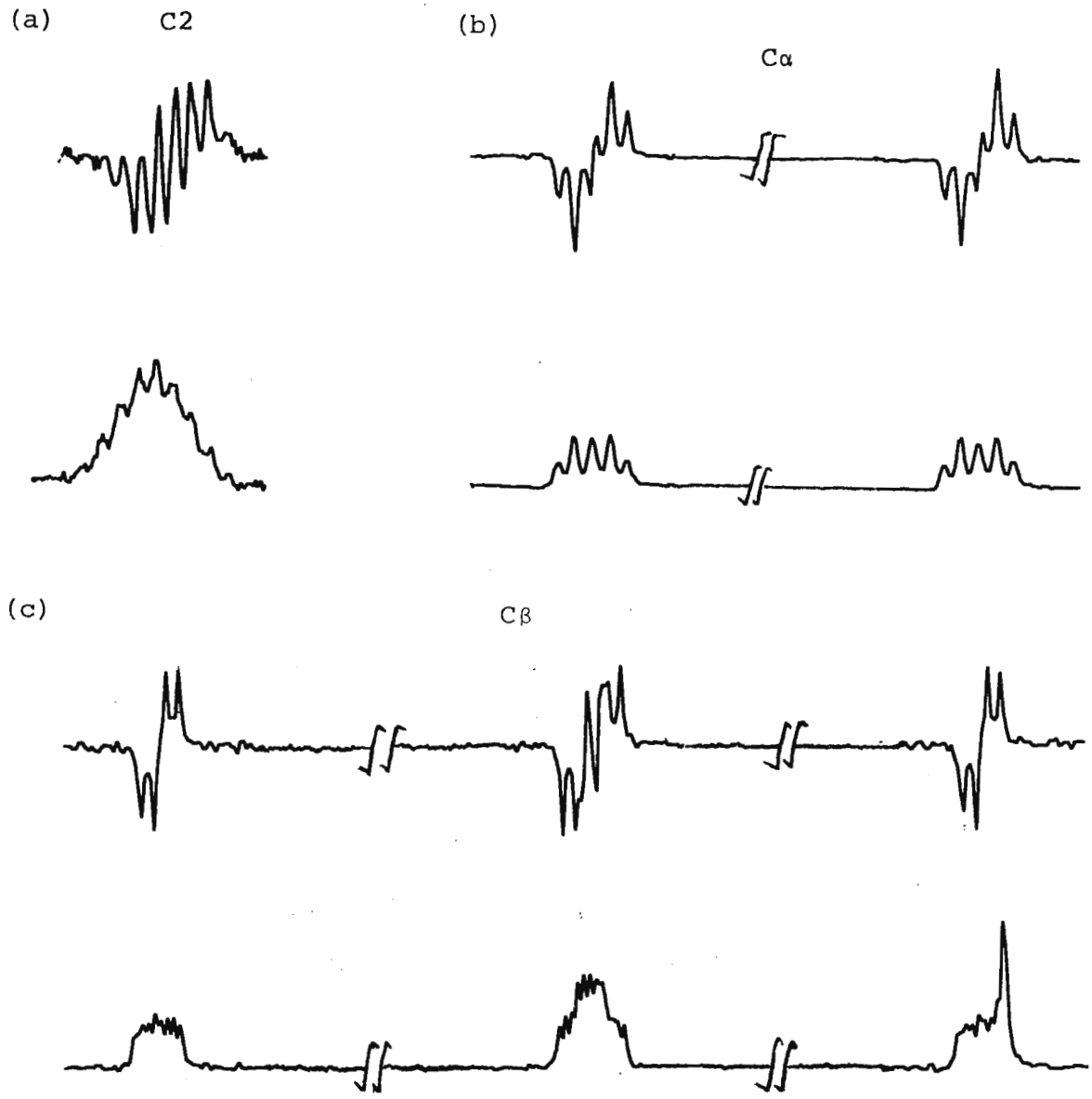
Figure 2.



Please credit this letter to Prof. M. Anteunis.

Yours Sincerely,

Milos BUDESINSKY

Frans A. BORREMANS

Institute of Organic Chemistry
and Biochemistry
Czechoslovak Academy of Sciences
166 10 PRAGUE 6

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School of Studies in Chemistry

Professor B.L.Shapiro, TAMUNMR Newsletter,
Department of Chemistry, Texas A & M University,
College Station, TEXAS 77843.
U.S.A.

18th January, 1979

Dear Professor Shapiro,

^{1}H AND ^{13}C NMR SPECTRA OF SUPERCRITICAL - GAS EXTRACTS OF COALS

With collaborators at the (British) National Coal Board Coal Research Establishment and at Ankara University (Turkey) we have recently compared the nature of products which have been obtained from British coals and Turkish lignites by the novel approach of extracting with supercritical gases.

^{13}C - NMR spectra of the aliphatic fractions[1] of the extracts reveal the presence of isoprenoidal hydrocarbons; these are important as geochemical markers since they are derived from the chlorophyll pigment of the original plant material.

Statistical structural analysis of the (more complex) aromatic fractions was based on ^{1}H-NMR-determined hydrogen distributions and on quantitative ^{13}C-NMR spectra recorded[2] with gated decoupling and in presence of $Cr(acac)_3$; the scheme employed is developed from that originally applied by Bartle and Smith to coal derivatives but now modified[3] to give a more realistic account of substituent alkyl and hydroaromatic groups.

In the ^{13}C spectra of oxygen-rich fractions, bands between 148 and 168 p.p.m. are assigned to carbon bonded to phenolic OH and aromatic-ether oxygen, with confirmatory bands between 100-115 p.p.m. from aromatic C-H ortho to such groups. No signals from C=O were detected. Superposed on the rather broad aliphatic carbon bands in ^{13}C spectra of the lignite-extract aromatic fractions[4] are sharp lines at 14,23,32 and 29.5 p.p.m. corresponding, respectively, to the 1,2,3 and 5 (or further) carbons of long alkyl-chain substituents. Structural analysis suggests open-chain structures with 2-3 aromatic rings per cluster for the British coal extracts[3], but single-aromatic-ring structures for extracts of lignites[4].

Yours sincerely,

K. D. Bartle Denry Jones Hooshang Pakdel

K.D.Bartle (Dept.of Phys.Chem. Leeds University)
D.W.Jones
H.Pakdel
C.E.Snape (N.C.B.Coal Research Establishment)

1. K.D.Bartle, D.W.Jones and H.Pakdel in "Molecular Spectroscopy",A.R.West(ed) (Heyden, 1977), p.127.
2. W.R.Ladner and C.E.Snape, Fuel, 57, 658 (1978).
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4. K.D.Bartle, A.Çalimli, D.W.Jones, R.S.Matthews, A.Olcay, H.Pakdel and T.Tugrul, Fuel, in the press.

THE UNIVERSITY OF NEW ENGLAND
ARMIDALE, N.S.W. 2351.
Department of Organic Chemistry

19th January, 1979

Professor B. Shapiro,
Department of Chemistry,
Texas A&M University,
COLLEGE STATION,
Texas 77843, U.S.A.

Dear Professor Shapiro,

Subject: THEORETICAL VERIFICATION OF A P.M.R. CONFORMATIONAL CONCLUSION

Being preoccupied with the matters described below, I was not delighted to see your pink form although I have often been intrigued by other writers' comments about it! I hope the present contribution will meet my immediate obligation.

As mentioned in Newsletter No.231 we have been interested for many years in p.m.r. spectra and conformation of lactones. By the methods described (1), we derived proportionality constants for Karplus-type equations in these systems and concluded the cis-dihedral angle for vicinal protons (2,3- or 3,4-) in butyrolactones in solution was 35-40°, an envelope conformation being most likely, as had been observed by X-ray determinations on a number of solid lactones. We also concluded that a 3-phenyl substituent preferred the equatorial position whereas a 3-hydroxyl substituent preferred the axial position.

During the past two years or so, in association with Dr Leo Radom, I have made a number of ab initio SCFMO calculations on preferred conformations of various systems, and have recently been carrying out a partial optimisation of the geometry of butyrolactone. I am pleased to report that the cis-dihedral angles mentioned above are calculated to have optimum values close to 35°! In an attempt further to verify the experimental conclusions, the next stage will be to calculate by the finite-perturbation method coupling constants for the optimised geometry. I hope also to verify the preferred orientation of the 3-hydroxyl substituent, but ab initio calculations on these systems, even at the minimal STO-3G level, are very expensive of computer time and it will not be practicable to refine the results much beyond the present stage nor to carry out such a calculation for the 3-phenyl substituent.

Yours sincerely,

N.V. Riggs

N.V. Riggs
Professor of Organic Chemistry

(1) Tetrahedron Letters, 1964, 2911-17;
1967, 5113-17, 5119-22.
Aust. J. Chem., 1971, 24, 1643-58, 1659-66.

245-49

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Telegrams Govchem London
Telephone 01-928 7900 ext 649

Professor B L Shapiro
Department of Chemistry
Texas A & M University
College Station
TEXAS 77845
USA

Your reference

Our reference

Date 21 November 1978

Dear Professor Shapiro

EXAMINATION OF STREPTOMYCIN/DIHYDROSTREPTOMYCIN MEDICINALS BY NMR

Streptomycin and dihydrostreptomycin are aminoglycoside antibiotics used mainly as their sulphate salts, in medicinal and veterinary preparations (1-3). Veterinary products consisting of a mixture of the two have presented problems in analysis; thin-layer chromatography does not provide a satisfactory identification since the compounds are not resolved when present as a mixture (4,5) and biological assays also fail to distinguish between them. Quantitative colorimetric methods (6,7) are known for streptomycin or total guanidine-containing aminoglycosides but not for dihydrostreptomycin.

While qualitative analysis is readily achieved by ^{13}C nmr (Fig 1), a fully quantitative method using a nOe suppression sequence looks as though it will require rather lengthy spectrum accumulations. However, quantitative analysis may be achieved by ^{1}H nmr. At 60 MHz their spectra are identical for quantitative purposes apart from a singlet signal at $\delta = 5.02$ due to the hydrated "aldehyde" group in streptomycin (Fig 2). The signals at $\delta = 5.26$ and 5.54 are due to protons H_1 and H_9 in both streptomycin and dihydrostreptomycin (nomenclature as in 8). These integrals give the quantity of streptomycin and the sum of streptomycin and dihydrostreptomycin present (Fig 3). For accurate integration it is necessary to reduce the HDO signal by first deuterating the exchangeable proton sites by freeze drying the compounds from a D_2O solution before redissolving in D_2O for nmr measurement.

This work will be the subject of a forthcoming paper.

P Bottomley — Mrs E M May — C P Richards

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2 British Pharmacopoeia (1973)
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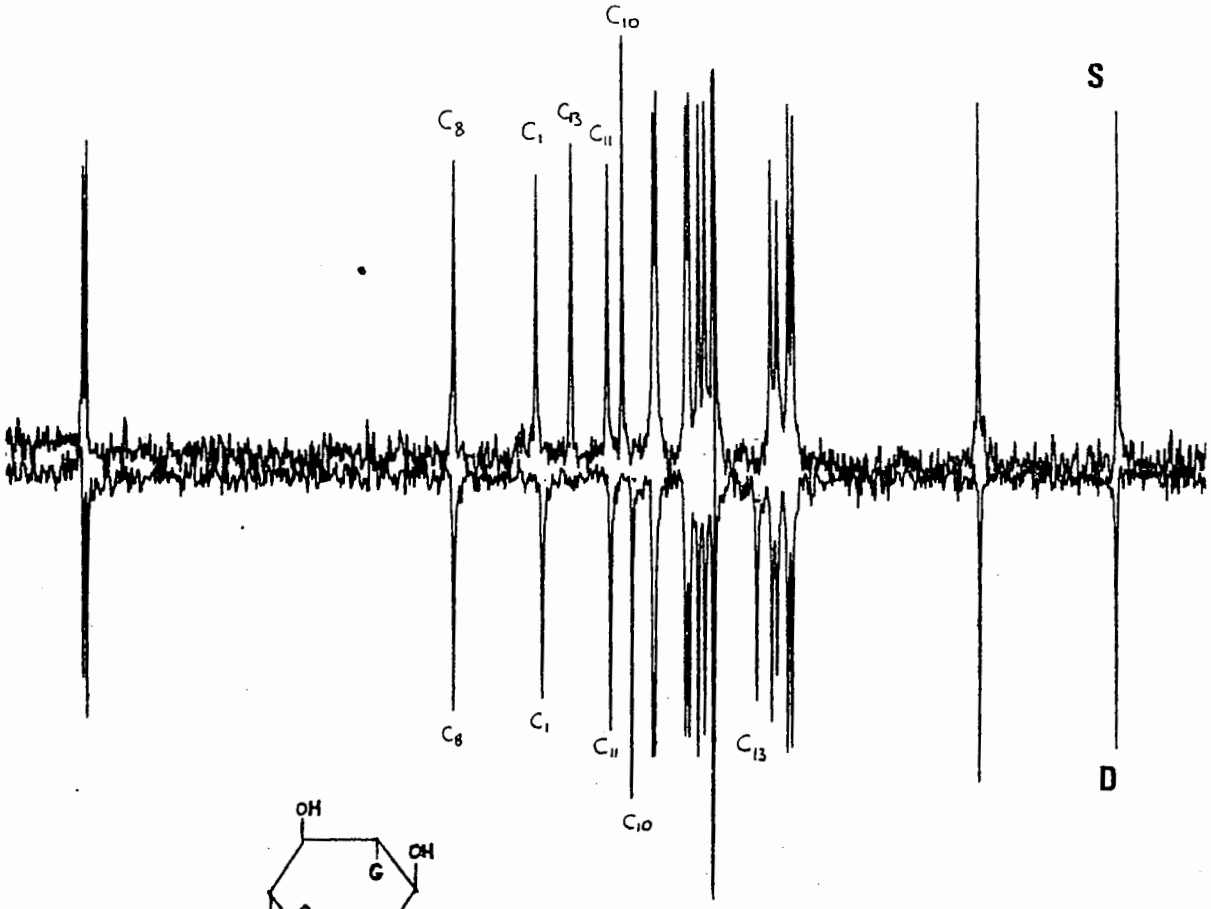
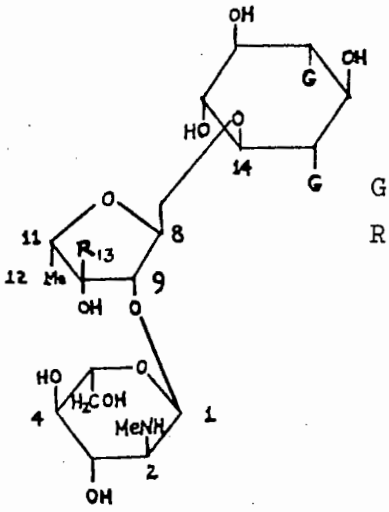
Fig 1 25 MHz ^{13}C nmr spectra of streptomycin (S), dihydrostreptomycin (D), and their mixture (SD)





G = guanidine

R = CHO in streptomycin
= CH_2OH in dihydrostreptomycin

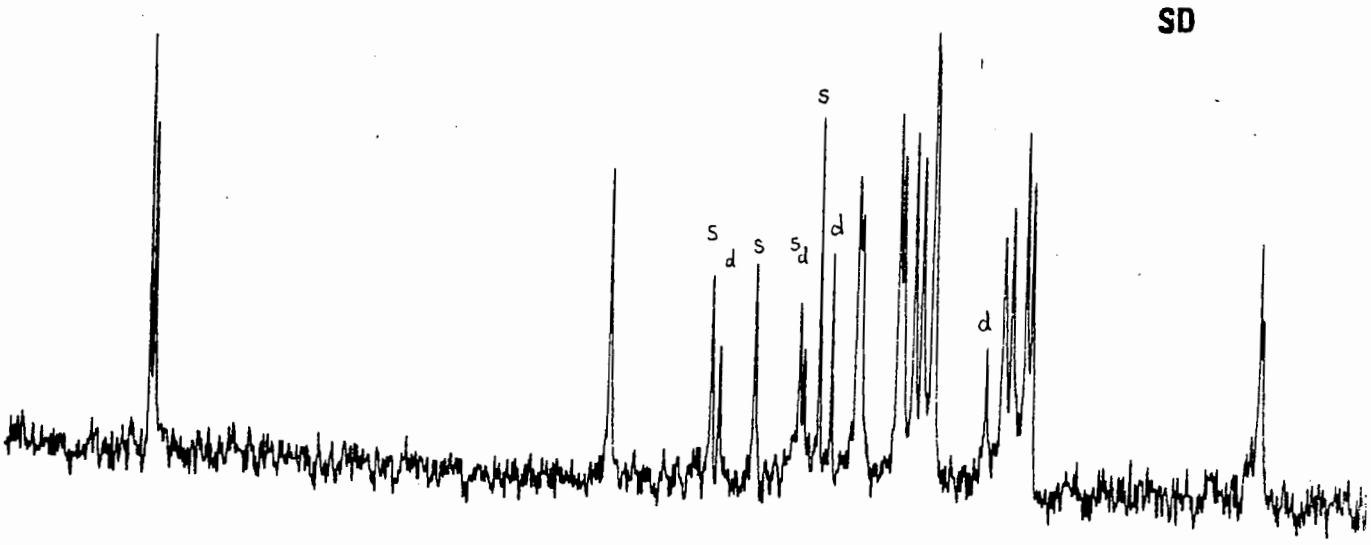


Fig 2 60 MHz ^{1}H nmr spectrum of streptomycin sulphate

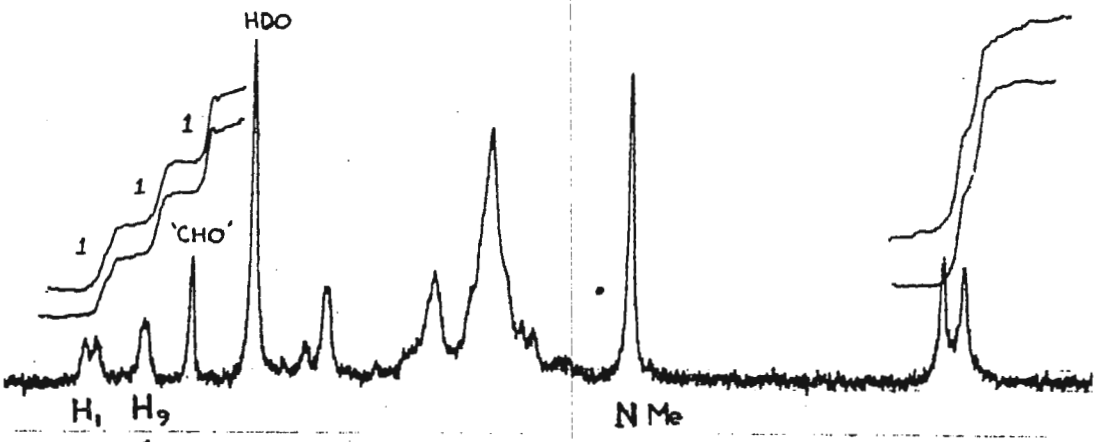
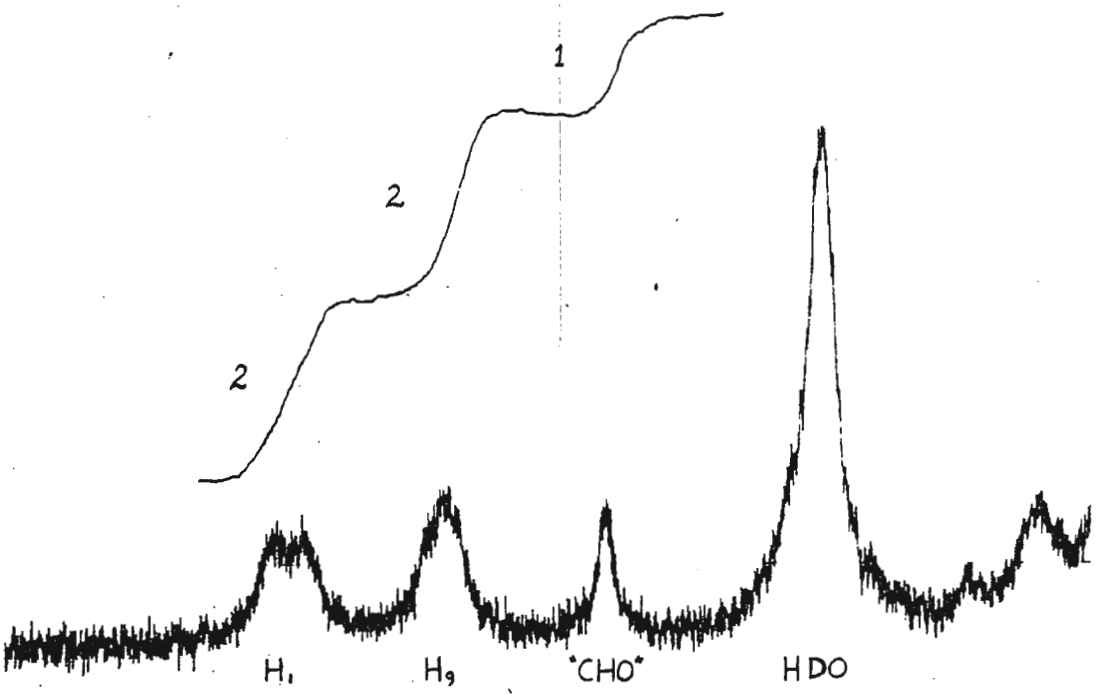


Fig 3 60 MHz ^{1}H nmr spectrum of an equimolar mixture of streptomycin and dihydrostreptomycin sulphates



GESELLSCHAFT ZUR FÖRDERUNG DER SPEKTROCHEMIE
UND ANGEWANDTEN SPEKTROSKOPIE E. V.
INSTITUT FÜR SPEKTROCHEMIE

From:

Dr. R. Gerhards c/o
Postanschrift: Institut für Spektrochemie, Postfach 770, 4600 Dortmund 1

Professor B.L. Shapiro

Chemistry Department

Texas A & M University

College Station, Texas 77843 / USA

Bunsen-Kirchhoff-Straße 11
(Abzweig Ardeystraße)
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Ihre Zeichen	Ihre Nachricht vom	Unsere Zeichen	
		Ger/Mas.	27.1.1979

Betreff: Title: 'A fast, iterative fitting routine of relaxation data from inversion recovery experiments

Dear Professor Shapiro,

It has been shown by a lot of research groups that ^{13}C-NMR-longitudinal relaxation times T_1 can be a useful tool for structure elucidation and determination of conformation and configuration of organic molecules.

But the necessary condition for a correct interpretation of T_1 is, that correct values for T_1 have been determined. Wrong values can be caused by inadequate measuring routines (pulse-width, paramagnetic molecules in the sample, e.g.), which is obvious to every experimentator, but also, and this is not in everybody's mind, by use of common calculating method of T_1, where the measured relaxation data have to be transformed in a semi-logarithmic system. A closer look regarding the error possibilities of the usual calculating routine is given elsewhere (1, 2).

To avoid these errors it is necessary to fit the measured data of a relaxation experiment in the untransformed system, where the relaxation test point $M(t_i)$ can be described by eq. 1

$$M(t_i) = M_o(1-(1-\cos\alpha)\cdot\exp(-t_i/T_1)) \qquad (1)$$

with $\alpha = 180^o$ for the inversion recovery method
and $\alpha = 90^o$ for all saturation experiments.

Due to the non-polynominal form of eq. 1, the relaxation parameters M_o, T_1 and α then can only be calculated in an iterative regression procedure as they are described, for example, by Leipert and Marquardt (3), Marquardt (4) and by our group (2).

In our paper we developed the calculating procedure, following the method of Stevens (5) and Hiorns (6) to get the maximum likelihood values of the relaxation parameters. This procedure has the advantage that only one parameter, namely T_1, has to be iterated explicitly, while the others are found directly when T_1 has its correct value. Using this procedure it is very simple to calculate confidence intervals for all relaxation parameters without any further effort.

If the experimental conditions are chosen well, it is no longer necessary to calculate the parameter α, because it should be 90° for a saturation experiment and 180° for the inversion-recovery method. So we used the described method only for testing whether the confidence interval of α includes the value 90°, as we used a saturation-relaxation experiment.

For calculating the relaxation parameters M_o and T_1 we then fitted the relaxation data by a similar regression routine to a more simple relaxation function (eq. 2) with only two parameters,

$$M(t) = M_o \cdot (1-\exp(-t(T_1)) \qquad (2)$$

During the past years we heard from several colleagues that it would be helpful if there would be a similar routine to fit relaxation data of inversion-recovery experiments that can be described by eq. 3, when it is justified that α is 180° (for example by fitting the parameter of eq. 1)

$$M(t) = M_o \cdot (1-2\cdot\exp(-t/T_1)) \qquad (3)$$

So here is the procedure:

If we define $r = \exp(-1/T_1)$ one has to solve with an arbitrary value of r ($0<r<1$) the following matrix system (eq. 4), where all sums have to be calculated over the number n of the test points along the relaxation function

$$\begin{pmatrix} M_o \\ 2\cdot M_o\cdot\delta r \end{pmatrix} = \begin{pmatrix} a & b \\ b & c \end{pmatrix}^{-1} \cdot \begin{pmatrix} \sum M_i\cdot(1.2\cdot r^{t_i}) \\ \sum M_i\cdot t_i\cdot 2\cdot r^{t_i-1} \end{pmatrix} \qquad (4)$$

with $a = \sum(1-2\cdot r^{t_i})^2$, $b = -\sum t_i\cdot 2\cdot r^{t_i-1}\cdot(1-2\cdot r^{t_i})$,

$c = \sum t_i^2\cdot 2\cdot r^{t_i-2}$

The value of r in the next iteration cycle is then determined by the relation $r_{new} = r_{old} + \delta r$. The iteration is stopped when δr is smaller than 10^{-8}. The relaxation parameter M_o then can be taken directly from the solution of the last matrix equation of the iteration, and T_1 is given by $T_1 = -1/\ln(r)$.

The variance of the fitted relaxation data can be calculated in the usual manner (eq. 5)

$$v = \frac{[M_i - M_o \cdot (1-2 \cdot r^{t_i})]^2}{n-2} \qquad (5)$$

The standard errors of the parameter r (respectively T_1) and M_o then are given by eq. 6, using the abbreviation from eq. 4

$$s_{M_o} = \sqrt{a \cdot v} \qquad s_r = \sqrt{c \cdot v/(2 \cdot M_o)} \qquad (6)$$

This routine is simply programmable, even on a dedicated computer of a NMR-equipment. A FTN-IV procedure is available on request.

Sincerely Yours,

R. Gerhards

Dr. R. Gerhards (7)

1. G.C. Levy, I.R. Peat, J. Magn. Resonance 18, 500 (1975)
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4. D.W. Marquardt, Technometrics 12, 591 (1970)
5. W.L. Stevens, Biometrics 7, 247 (1951)
6. R.W. Hiorns, "The fitting of Growth and Allied Curves", University Press, Cambridge (1965)

7. The basis of the procedure presented in this paper was developed during the course of a Doctor's Thesis under the kind attention of Prof. Dr. G. Bergmann and Dr. W. Dietrich, at the 'Lehrstuhl für Analytische Chemie, Ruhr Universität Bochum, Postfach 10 21 48, D-4630 Bochum 1, West Germany.

245-55

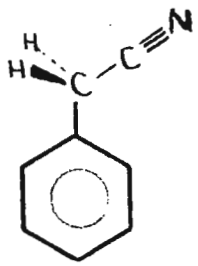
THE UNIVERSITY OF WINNIPEG
WINNIPEG, CANADA R3B 2E9

January 18, 1979

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station
Texas 77843, U.S.A.

Dear Barry:

We have recently completed a ^{13}C nmr study of benzyl cyanide (I). The rotation of the molecule was modelled on the diffusion of a prolate spheroid and the following features were deduced:



(I)

(1) rotation of the aromatic ring about the long axis of the molecule is about 3 times faster than rotation of this axis, (2) rotation of the $-CH_2CN$ group about the long axis is about 1.5 times faster than the aromatic ring, and (3) activation energies associated with the temperature dependence of the ^{13}C-^{1}H dipolar relaxation rates agree with the hydrodynamical prediction of 3.6 kcal/mole associated with the temperature dependence of the ratio shear viscosity/temperature.

The temperature dependence of the ^{13}C T_1's of the cyano carbon in I may be of interest to some readers (see figure 1). $^{1}3C$-^{1}H dipole-dipole relaxation is the most important mechanism at the lowest temperatures studied, while spin-rotation coupling dominates at the highest temperature. Chemical shift anisotropy and ^{14}N-^{13}C dipolar coupling are also expected to make a contribution to T_1^{other}.

Although it makes a negligible contribution to T_1, scalar coupling to ^{14}N is very effective in the relaxation of the transverse component of the cyano ^{13}C magnetization. The ^{13}C line width corrected for magnetic field inhomogeneity varied from about 1.2 Hz at 30°C to 2.9 Hz at 170°C. These values are in fair agreement with values calculated assuming $^{1}J(^{15}N,^{13}C) \simeq -16$Hz and using available ^{14}N nmr linewidths (1) together with standard formulae (eq. 127, p. 311 of ref. 2).

Finally it is of interest to point out that the absolute value of $^{2}J(^{13}\underline{C}N, ^{13}\underline{C})$ in I is only 3.5 Hz. This is substantially smaller than the

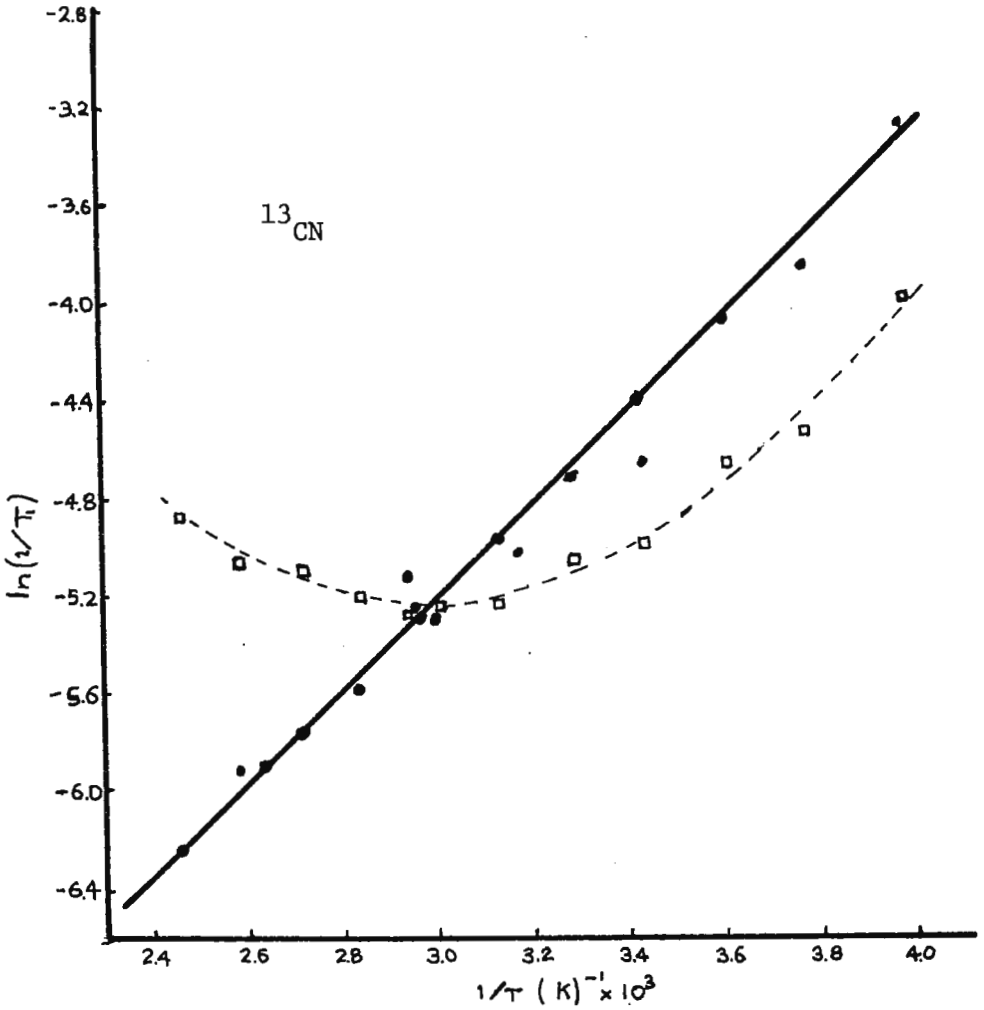


Figure 1 The temperature dependence of the observed relaxation rates for the cyano $^{13}C_1$ in benzyl cyanide: the circles and solid line represent the $^{13}C-^{1}H$ dipolar component, and the squares and broken line represent the component due to other mechanisms.

value of 33.0 Hz reported for $^{2}J(^{13}\underline{C}N, ^{13}\underline{C})$ in propionitrile.

Best wishes in the New Year.

Sincerely,

Rod

Rod Wasylishen Brian Pettitt

1) D. Wallach. J. Phys. Chem. 73, 307 (1969).

2) G. A. Gray, G. E. Maciel, and P. D. Ellis, J. Mag. Res. 1, 407 (1969).

3) A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, London and New York (1961).

245-57

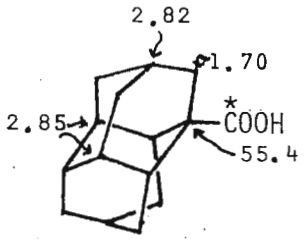
January 24, 1979

Dr. B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843

North Texas State University
Denton, Texas 76203
Department of Chemistry

Dear Barry:

The original observation[1] that vicinal carbon 13-carbon 13 coupling constants do not exhibit a maximum in compounds at a dihedral angle of 180°, but instead at about 160°, was shown to be due by the particular choice of model compounds used in this study. Specifically, through-space interactions in the adamantane and cyclohexane system were responsible for affecting the vicinal coupling constant at a dihedral angle near 180°. The particular geometry of the adamantane skeletons suggested that perhaps even more "anomalous" results would be seen in a system that had the possibility of a larger number of through-space effects. Accordingly, we synthesized congressannecarboxylic acid, labeled with C-13 in the carboxyl position, for a C-13 nmr study. The coupling constants observed are marked in the structure below. It is to be noted that the vicinal coupling constant with a dihedral angle of 180°, both to positions 9 and 7, are less than 3Hz, while this corresponding coupling constant in adamantane carboxylic acid is 3.6 Hz, and can be as large as 5.6 Hz (in 7-norbornane carboxylic acid[1]). Hence, it appears that the value of vicinal carbon-carbon coupling constants are not as reliable an indicator of conformation as proton-proton coupling constants have proven to be.



(All carbons to which values are not assigned were not observed to couple, i.e., $|J| < 0.5$ Hz)

Sincerely yours,

James L. Marshall
Professor of Chemistry

REFERENCES

1. J.L. Marshall, and D.E. Miiller, J. Amer. Chem. Soc., 95, 8305 (1973).
2. M. Barfield, S.A. Conn, J.L. Marshall, and D.E. Miiller, J. Amer. Chem. Soc., 98, 6253 (1976).
3. M. Barfield, J.L. Marshall, E.D. Canada, and M.R. Willcott, III, J. Amer. Chem. Soc., 100, 7075 (1978).

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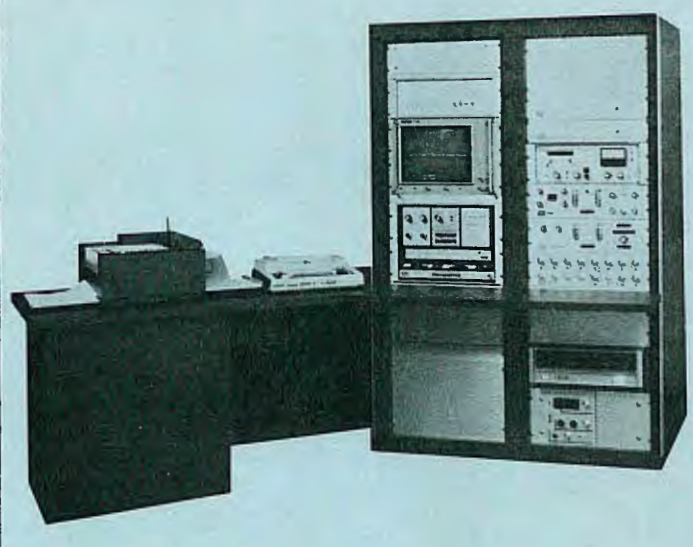

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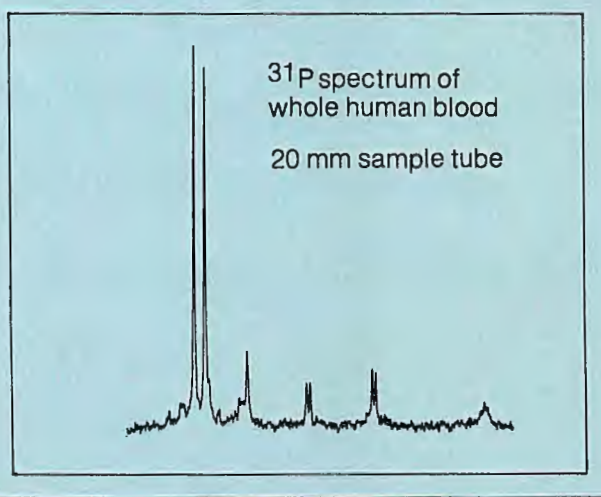

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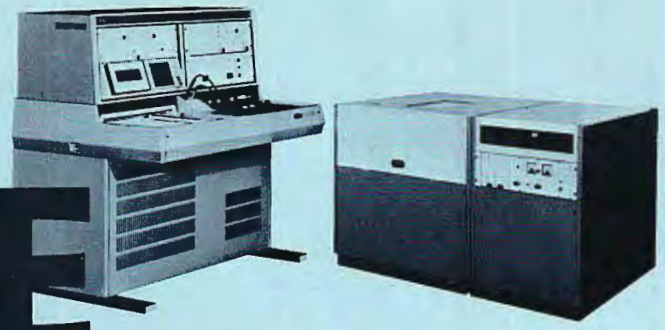

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