TEXAS A&M UNIVERSITY

NMR NEWSLETTER

NO. 310

JULY 1984

DEADLINE DATES

No. 312 ------ 3 September 1984

No. 313 -------- 1 October 1984

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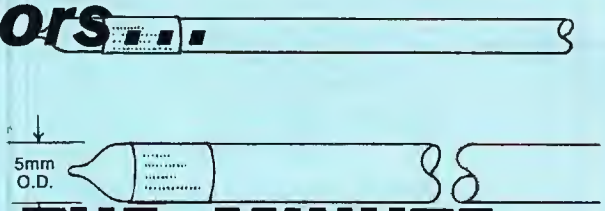

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	WGH-55	20% Orthodichlorobenzene + 5% TMS in Acetone-d,	Resolution	33.00
	WGH-61	95% Orthodichlorobenzene + 5% TMS	Resolution	
	WGH-65	70% Orthodichlorobenzene in Deuterated Chloroform	Resolution	33.00
	WGH-69	30% Orthodichlorobenzene in Acetone-d,	Resolution	33.00
	WGH-63	30% Orthodichlorobenzene in Deuterated Chloroform	Resolution	31.00
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All Newsletter Correspondence
Should be Addressed to:

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

AUTHOR INDEX ---------- TAMU NMR NEWSLETTER NO. 310, JULY 1984

UNIVERSITY OF KENTUCKY

LEXINGTON, KENTUCKY 40506-0055

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DEPARTMENT OF CHEMISTRY
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FIRST ANNOUNCEMENT

16TH SOUTHEASTERN MAGNETIC RESONANCE CONFERENCE

UNIVERSITY OF KENTUCKY

LEXINGTON, KENTUCKY 40506

OCTOBER 3 - 5, 1984

We have planned on an exciting 16th SEMRC program of invited symposia and contributed posters on ESR and NMR. A tentative list of invited speakers is attached. We hope that you will start to make plans now to attend and perhaps contribute posters on your work. A follow-up mailing in August/September to those who return the attached form will solicit your registration and abstracts. As in the past, registration and a mixer will be held on Wednesday evening (October 3rd) and the technical program will be held Thursday and Friday (October 4th, 5th). The Blue Grass region will be lovely in October. We hope to see you here.

With warm regards,

D. Allan Butterfield, Ph.D.
Professor, Co-Chairman
16th SEMRC

Stanford L. Smith, Ph.D.
Professor, Co-Chairman
16th SEMRC

TENTATIVE LIST OF INVITED SPEAKERS

ESR

James Bolton, Univ. of Western Ontario
Jack Peisach, Albert Einstein/Bell Labs
Lowell Kispert, Univ. of Alabama
Edward Janzen, Univ. of Guelph
Donald B. Chesnut, Duke University
Colin Cignell, NIEHS
Allan Butterfield, Univ. of Kentucky

NMR

Harry Dorn, VPI
Jerome Ackerman, Univ. of Cincinnati
Richard Wittebort, Univ. of Louisville
Robert Santini, Purdue University
Paul Ellis, Univ. of South Carolina
Katherine Scott, Univ. of Florida
Stanford Smith, Univ. of Kentucky
Allen Carr, Univ. of Kentucky

16TH SEMRC

UNIVERSITY OF KENTUCKY

OCTOBER 3-5, 1984

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_____ I tentatively plan to present a poster paper of tentative title_____.

_____ I tentatively plan to travel to Lexington

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___ by car

___ by other _____

_____ I will not be attending the 16th SEMRC.

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Please return to:

16th SEMRC
Prof. D. A. Butterfield
Prof. S. L. Smith
Department of Chemistry
University of Kentucky
Lexington, Kentucky 40506-0055

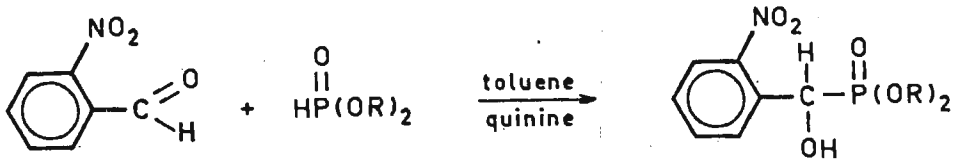
Dr. B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station
Texas 77843
USA

Groningen, May 29 1984

Dear Professor Shapiro

Determination of the enantiomeric excess of chiral acids by ^{31}P-NMR

Last year we discovered a good method to synthesize optically active α-hydroxy dialkylfosfonates using quinine as a catalyst.[1] The enantiomeric excess of the chiral alcohols was determined by NMR using Mosher reagent.[2]



1. R = Me
2. R = i-Pr

In the ^{19}F-NMR we did not always find well separated signals for both diastereomers. However, we always obtained beautifully separated signals in the ^{31}P-NMR spectrum. Both the ^{19}F-NMR and ^{31}P-NMR spectra of a diastereomeric mixture of Moscher[2] derivatives of 2 are given in figure 1. We thought that optically pure 1 might be a potential reagent for the ee-determination of chiral acids, using ^{31}P-NMR. This proved to be the case. We derivatized 1 with a number of racemic acid chlorides and found in most cases well separated signals. The spectra were run at 80.099 MHz (^{31}P) and 188.217 MHz (^{19}F) on our Nicolet NT-200 instrument.
Please credit this contribution to the subscription of Dr. W.D. Weringa.

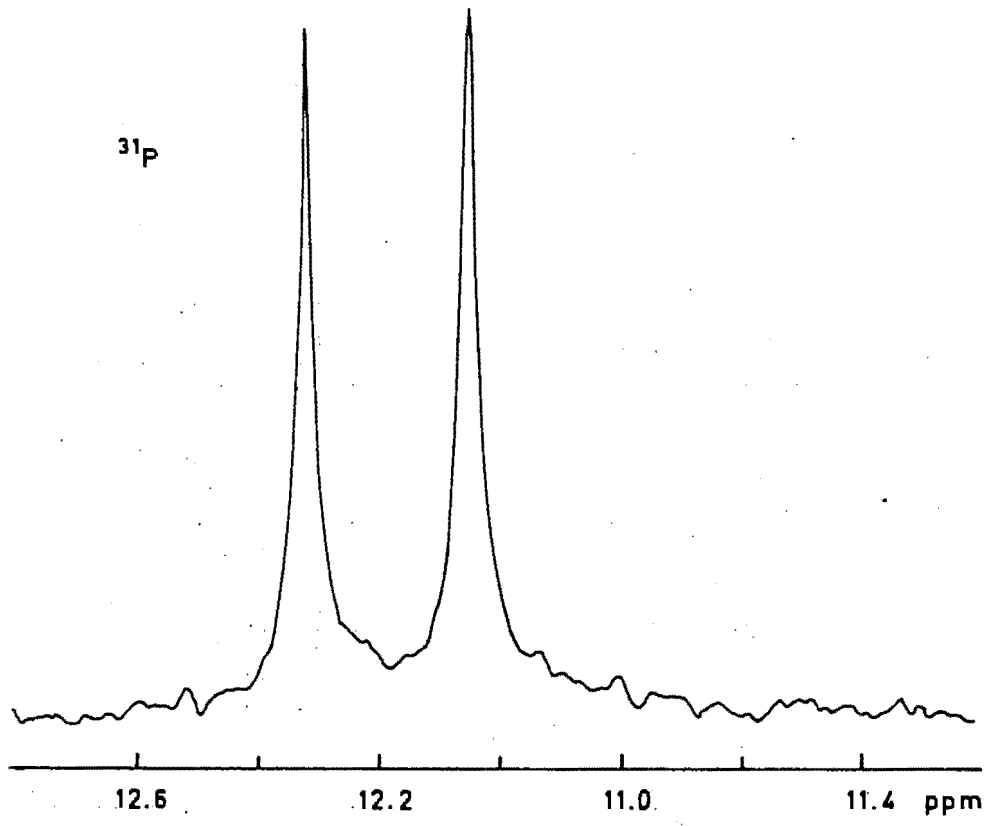
1. H. Wynberg, A.A. Smaardijk, Tetrahedron Lett., 1983, 24, 5899.
2. J.A. Dale, D.L. Dull, H.S. Mosher, J. Org. Chem., 1969, 34, 2543.

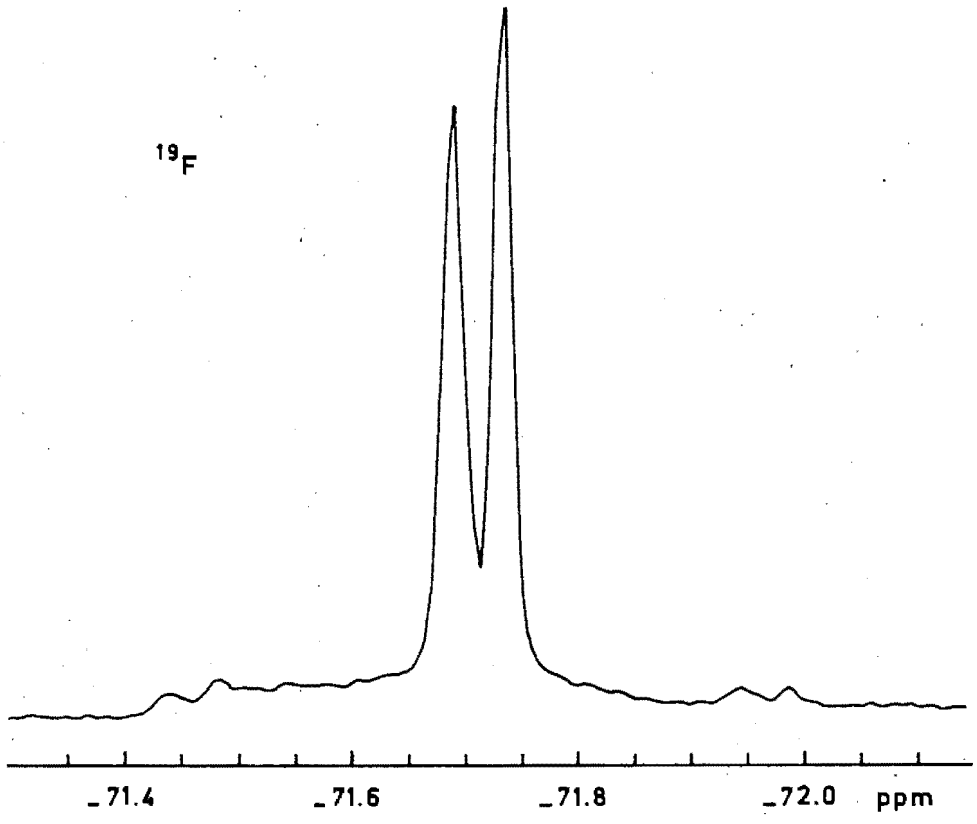
Sincerely yours,

A.A. Smaardijk

Drs. A.A. Smaardijk

Fig. 1





310-5

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
McCORMICK ROAD
CHARLOTTESVILLE, VIRGINIA 22901

June 22, 1984

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

Dear Dr. Shapiro:

Postdoctoral positions are presently available in our research group which I would appreciate being brought to the attention of any potential candidate. The salary stipend is $15,000 for the first year with the possibility of renewal. Projects of current interest include the following:

(i) ^{2}H, ^{31}P, and ^{13}C NMR studies of phospholipid bilayer membranes, and their interaction with proteins and cholesterol;

(ii) NMR relaxation studies of molecular dynamics in phospholipid bilayer membranes;

(iii) Synthesis and ^{2}H-labelling of polyunsaturated phospholipids;

(iv) Studies of rhodopsin function in recombinant membranes employing flash photolysis;

(v) Studies of membrane excitability in visual photoreceptors.

Our research group is highly interdisciplinary, and individuals with backgrounds in chemistry, biochemistry, physics, or electronics are encouraged to apply. Complete facilities are available in the Chemistry Department of the University of Virginia for these studies, including Nicolet NT-360 and JEOL FX-60Q Fourier transform NMR systems. Further expansion of our NMR facilities are planned in the future. Our laboratory is well equipped with standard chemical and biochemical preparatory equipment and facilities.

Interested persons should send a curriculum vitae together with three letters of recommendation to: Dr. M. F. Brown, Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. Further background information can be obtained from the following references:

1. M. F. Brown, J. Seelig, & U. Haeberlen, J. Chem. Phys. 70, 5045-5053 (1979)
2. M.D. Sefcik, J. Schaefer, E.O. Stejskal, R.A. McKay, J.F. Ellena, S.W. Dodd, & M.F. Brown, Biochem. Biophys. Res. Commun. 114, 1048-1055 (1983)
3. (a) M.F. Brown, J. Chem. Phys. 77, 1576-1599 (1982); (b) ibid. 80, 2808-2831 (1984a); (c) ibid. 80, 2832-2836 (1984b)
4. J.M. Beach, R.D. Pates, J.F. Ellena, & M.F. Brown, Biophys. J. 45, 292a (1984)
5. D.J. Siminovitch, M. Rance, K.R. Jeffrey, & M.F. Brown, J. Magn. Res. 58, 62-75 (1984)

With Best regards.

Yours sincerely,

Michael F. Brown

Michael F. Brown
Assistant Professor of Chemistry

MFB:ah

NATIONAL CANCER INSTITUTE
FREDERICK CANCER RESEARCH FACILITY
P.O. Box B, Frederick, Maryland 21701

June 18, 1984

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

Re: Effects of "excessive" line-broadening in 2-Dimensional NMR Spectroscopy.

Dear Barry,

We have recently analyzed the spectra of a number of molecules (i.e., cyclic peptides, fused aromatic hydrocarbons, mono and disaccharides) using modern 2D techniques such as 2D J, COSY (homocorrelation) and CSCM (heterocorrelation) spectroscopy. In many of these studies we were able to make assignments that would have been impossible just a few years ago.

In the course of processing our data we tried various tricks for enhancing or eliminating long range couplings. In this context we would like to caution scientists doing 2D spectroscopy that it is possible to lose information present in cross peaks by "excessive" line broadening, even though the chemical shift difference between coupled species is large. An example is shown in the Figure. While the explanation of the cross peak disappearance is straightforward the phenomenon may still present problems to the unwary.

Best regards,

Gwen

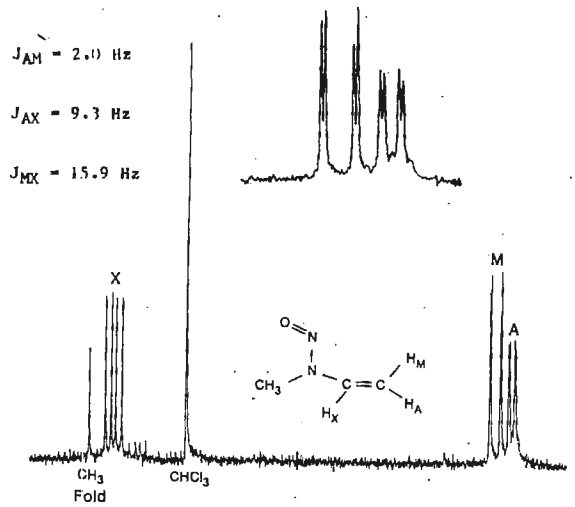
Jim

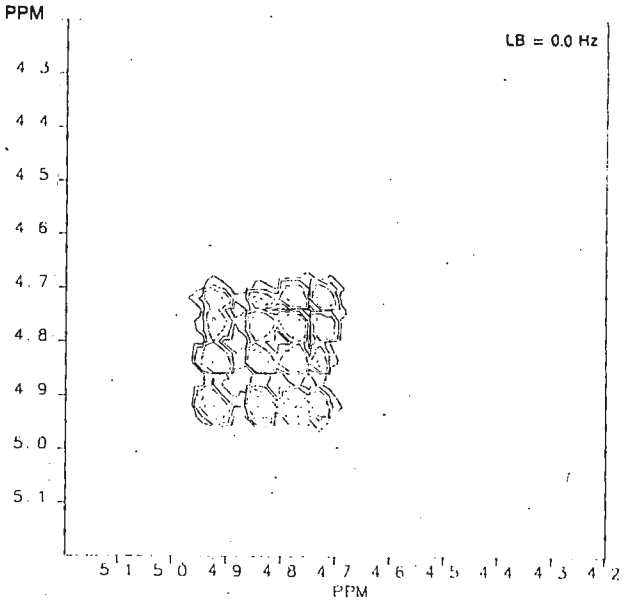
Gwendolyn N. Chmurny, Ph.D.
Bruce D. Hilton, Ph.D.
Chemical Synthesis and Analysis Laboratory
PRI, NCI-FCRF
P.O.Box B
Frederick, MD 21701

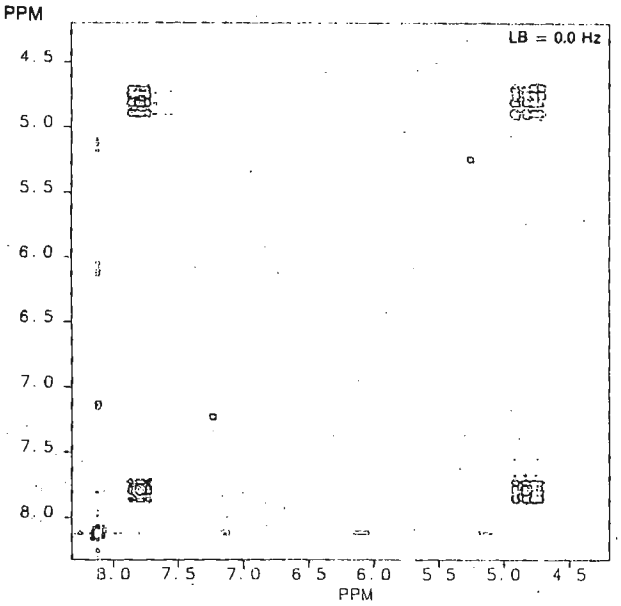
James A. Ferretti, Ph.D.
Laboratory of Chemistry
National Heart, Lung, and Blood Institute
National Institutes of Health
Building 10, Room 7N316
Bethesda, MD 20205

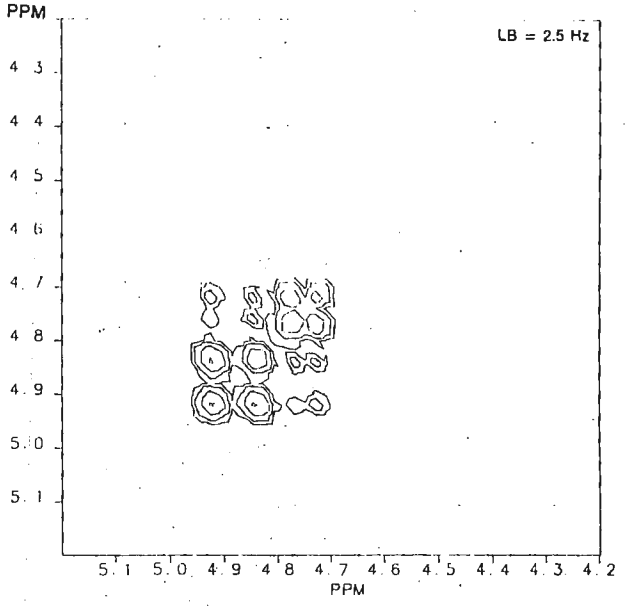
Please credit this contribution to the account of Dr. Gwendolyn N. Chmurny.

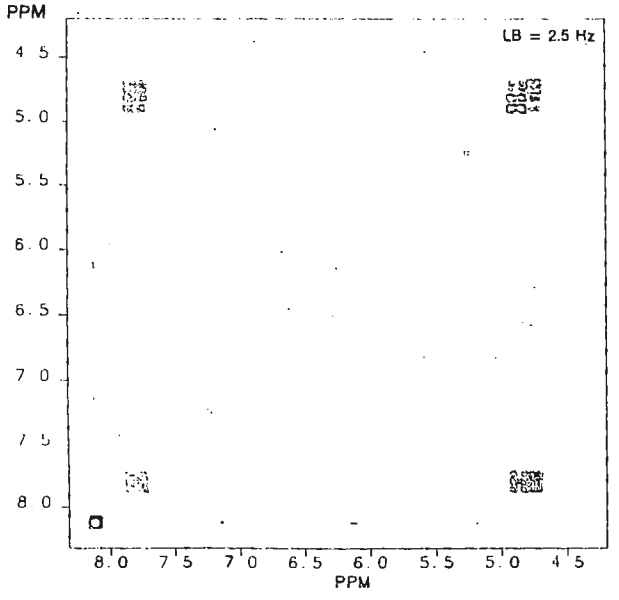
JAF:ap











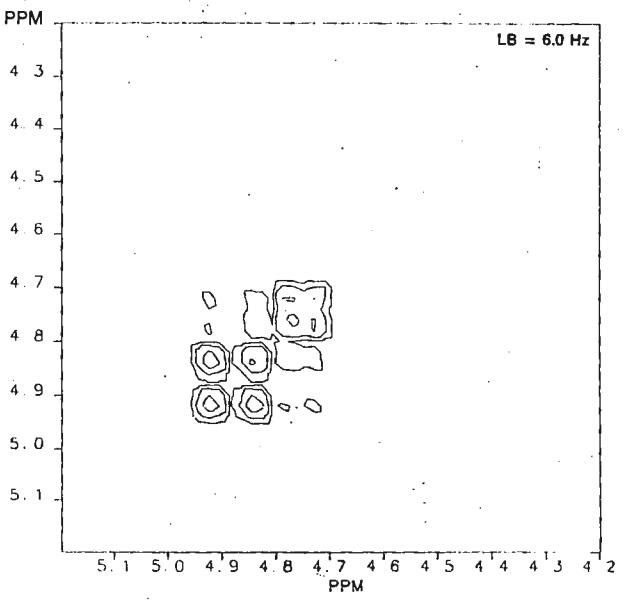


FIGURE: Contour plots with different amounts of line broadening of the COSY spectra of ca 17 mg of N-methyl-N-nitrosovinylamine in 0.5cc of $CDCl_3$. Note that the intensity of the cross peaks associated with the J_{AM} are greatly reduced with LB = 2.5 Hz. We are indebted to Dr. Robert J. Kupper of FCRF for providing us with this example and preparing the compound. The COSY spectra were taken on a Varian XL-200 spectrometer with an ADVANCE data system.

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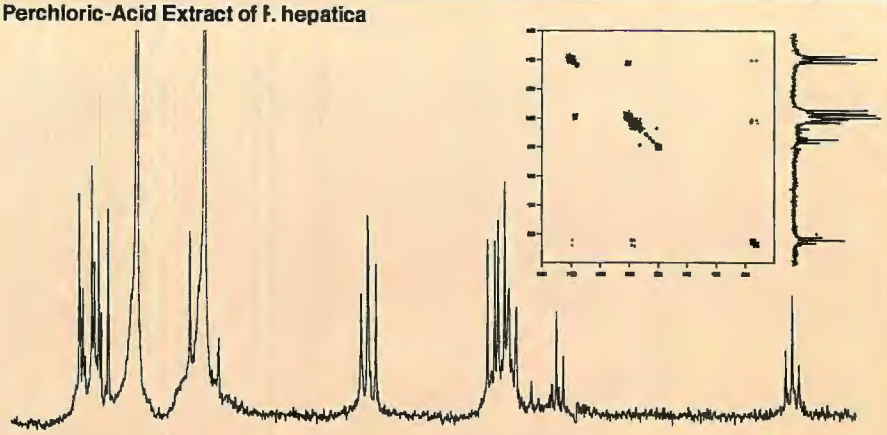
XL performance for demanding biological NMR studies

Recently, NMR has become an important tool for biochemists interested in studying metabolism *in vivo*. The applications shown on this page illustrate the broad range of capabilities required in an NMR spectrometer used in biological research. These capabilities demand superb sensitivity, flexibility in pulse programming, and software that permits taking advantage of available experiments and techniques.

Perchloric-Acid Extract of F. hepatica

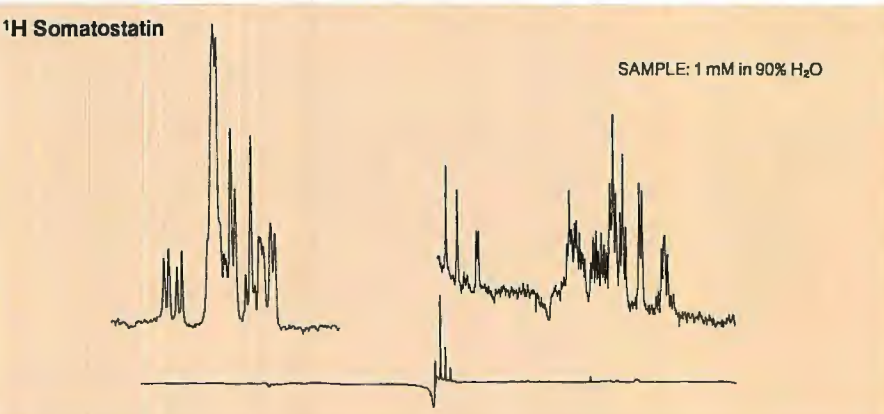


The high-sensitivity probes of the XL-200 allow spectra to be obtained from biologically relevant compounds at low concentration. The ^{31}P spectrum above is of a perchloric-acid extract of F. hepatica (bovine liver flukes) and was obtained in 4 hours (1500 transients) at 81 MHz, using a 10-mm probe. The spectrum has been resolution-enhanced to facilitate the identification of the ^{31}P-containing compounds present. The average concentrations of metabolites present in the sample are submillimolar.

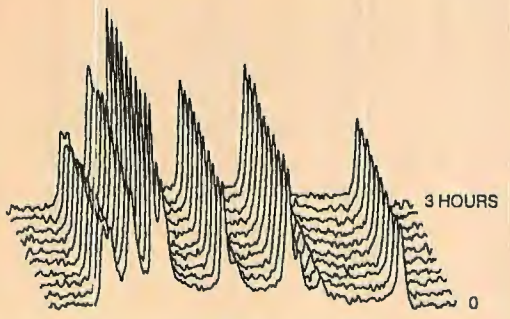
Two-dimensional NMR is a powerful method for analyzing complex mixtures. The contour plot shown above the spectrum is the result of a ^{31}P homonuclear shift correlation experiment carried out on a portion of the fluke extract using a 5-mm ^1H broadband switchable probe at 81 MHz. The total experiment time was approximately 12 hours. The experiment led to the discovery of a nucleotide pyrophosphate compound whose presence is indicated by the cross peaks between the P-α-nucleotide peaks and the peak at 800 Hz.

Biological NMR often requires the observation of protons in H_2O, particularly for observation of exchangeable protons. The strong signal from the solvent can be suppressed effectively by pulse sequences such as time-shared Redfield 2-1-4 or, as here, the Jump-and-Return pulse sequence. This XL-400 spectrum is the result of only 16 accumulations using a 1-millimolar solution. The aromatic expansion (rephased for upright presentation) shows the single-proton sensitivity that can be obtained in a half-minute period.

^1H Somatostatin

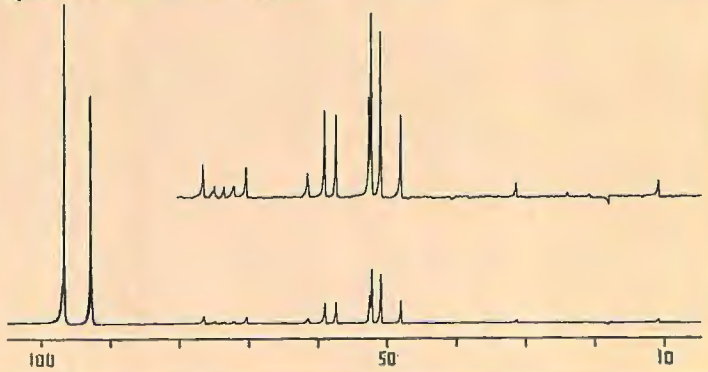


Perfusion of Tissue



Use of a modified 10-mm tube permits the NMR study of intact tissue while perfusing with temperature-controlled nutrient. No hardware modification of the spectrometer is necessary. The stacked plot shows the time course of ATP resonances during tissue perfusion with a nutrient medium and illustrates how tissue preparations can be maintained in a viable state during experiments. Insufficient or poor perfusion causes rapid degradation of the ATP and resultant cell or organism death. The ability to retain viability over many hours permits extensive study of metabolism in metabolic, nutrative, and cell research.

Spectrum of Perfusion Medium



NMR is a valuable tool for following metabolism in isotope labeling experiments. This spectrum is of the perfusion medium taken at the end of an experiment in which the bovine liver flukes (above) were perfused with (1-^{13}C) glucose. A large number of labeled species are formed as the (1-^{13}C) glucose is metabolized. Subsequent analysis of the sample using spectral editing pulse sequences and heteronuclear correlation experiments are essential for assignment of these resonances.

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ROHM AND HAAS COMPANY

June 19, 1984

Professor Barry Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

"Studies of Polymer Blend Compatibility by Solid State NMR"

Dear Professor Shapiro:

We have been doing some solid-state NMR experiments which can provide information on polymer blend compatibility. The solid state technique is useful because unlike FTIR/factor analysis a single sample can be examined, and of course much more chemical information is available than from Electron Microscopy.

The pulse sequence we use is described in J. Mag. Reson. 53, 486 (1983) by Zumbulyadis, who used it to suppress the signal from a Delrin rotor. The sequence consists of a cross-polarization experiment preceded by a 180 - tau on the protons. Thus we obtain a carbon spectrum of the sample in which the intensity of the carbon resonances will be determined by the T1 of the protons in the particular domain that each component is located in.

If we array the tau values as for a normal inversion-recovery experiment, we can use the software in our XL-200 to calculate the proton T1's associated with each observable carbon resonance. Taking spin diffusion into account, if we have domains formed which are larger than about 30nm then it should be possible to measure different proton T1's for the different domains.

One model system we have studied is a 50/50 blend of p(styrene) and p(vinyl methyl ether). When this blend is cast from toluene, a compatible blend is formed; casting from chloroform produces an incompatible blend.

Using the 56ppm methoxy resonance as a tag for the p(VME) and the 127ppm aryl resonance for p(styrene) we obtain the following proton T1's:

SOLVENT	p(VME)	p(STY)
chloroform	1.00 +/- 0.10	1.41 +/- 0.04 seconds
toluene	1.82 +/- 0.04	1.86 +/- 0.21 seconds

Professor Barry Shapiro
Texas A&M University

The different T1 values observed in the sample cast from chloroform indicate that the p(VME) and p(styrene) form domains; the sample is an incompatible blend. The relative magnitudes of the T1 values are also as expected: p(VME) has a glass transition temperature (Tg) of -5 C degrees, and should relax more quickly than the harder p(styrene) with its Tg of 110 C. On the other hand, the statistically identical T1 values observed for the sample cast from toluene are consistent with the fact that the blend is compatible. Both these results were verified by Electron Microscopy.

Sincerely,
Edward C. Greer
Edward C. Greer

Mobil Research and Development Corporation

June 14, 1984

RESEARCH DEPARTMENT
DALLAS RESEARCH DIVISION
P.O. BOX 819047
DALLAS, TEXAS 75381

13777 MIDWAY ROAD
DALLAS, TEXAS 75234

EUGENE L. JONES
MANAGER

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

Al-27 TO Si-29 SPIN-SPIN
COUPLING IN SOLID LOW ALBITE

Dear Barry:

Right after the Chemagnetics MAS solids accessory was installed on our JEOL FX-270 spectrometer in October, 1982, one of the first measurements I ran was of the Si-29 NMR spectrum of low albite from Amelia County, Virginia. The spectrum obtained was essentially the same as that shown in Figure 1B. Note that the peaks at -97 and -105 PPM appear to be doublets while the peak at -93 PPM is an apparent singlet with obvious shoulders. A similar spectrum was obtained from a low albite sample from Bristol County, Massachusetts. These results were mysterious as well as tantalizing because (1) published spectra obtained at other laboratories did not exhibit the apparent doublets and shoulders and (2) crystallographers assured me that there are only three different silicon sites in low albite. Also, we ran a number of experiments in order to determine that these splittings did not result from an unfortunate choice of experimental parameters.

The reported [Barron, Frost, Skjemstad, and Koppi, Nature 302, 49 (1983)] Si-29 splittings of comparable values at a similar magnetic field (300 MHz spectrometer) for other minerals from Mother Nature (kaolinite, dickite, and nacrite) served to heighten my interest in the cause. Measurements made on Amelia albite at 60 MHz field (Mark Sullivan of JEOL), at 200 MHz field (Mark Sullivan of JEOL and Kirk Schmitt of Mobil), and at 500 MHz field (Jeff Trewella of Mobil) indicated that the apparent splitting of the -97 and -105 PPM peaks appear to be independent of magnetic field. This strongly suggests that the apparent splitting in albite results from electron-coupled nuclear spin-spin interactions between Si-29 and Al-27 nuclei, when isotopic abundances are taken into consideration. Relevant to this suggestion is the reasonable assignment of the -93 PPM line to a silicon site which sees two aluminums while the -97 and -105 PPM lines see only one aluminum. Indeed, the shapes of the lines can be simulated by using reasonable J coupling constants (8 to 9 Hz) together with multiplet linewidths of varying values (13 to 26 Hz).

The spectra in Figure 1 illustrate several aspects of silicon-29 NMR spectra of natural samples. (1) The resolution increases with increase in magnetic field. (2) In highly-ordered alumino-silicates, narrow lines and spin-spin splittings can be observed. (3) Shimming of the magnetic field and magnetic field stability are very important in obtaining high resolution spectra at high magnetic fields when making measurements on spin-1/2 nuclei which have very long T_1's in highly ordered materials. As a corollary to (3), I suggest that the major NMR instrument manufacturers are grossly negligent in failing to install magnetic field locks in high-field superconductive MAS NMR spectrometers. My 270 MHz magnet, fortunately, appears to be exceptionally stable.

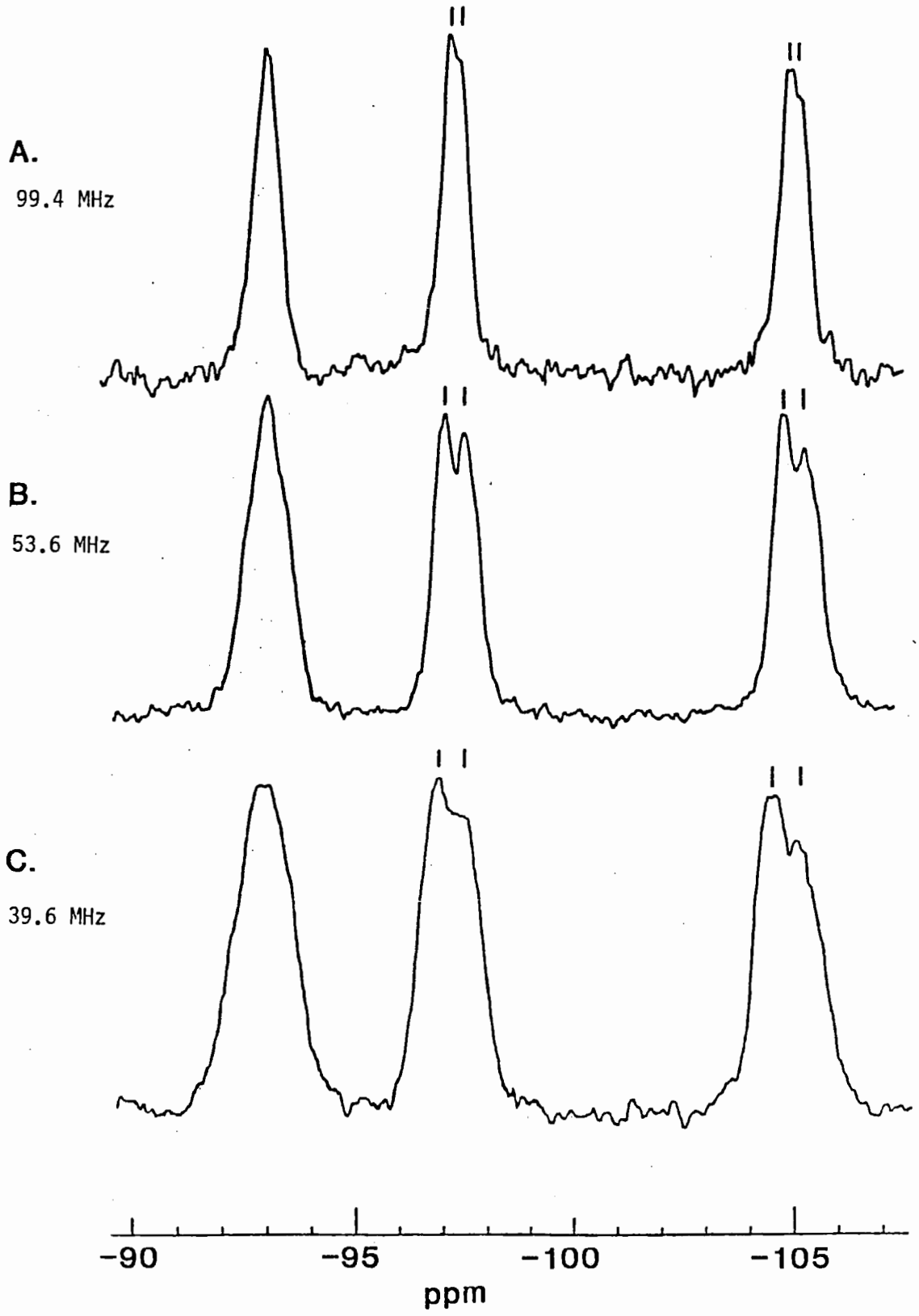
Sincerely,

Don

D. E. Woessner
Senior Research Associate

DEW:dpj
Enclosure

Figure 1. The silicon-29 MAS NMR spectra of Amelia albite at three different NMR frequencies.



DEPARTMENT OF HEALTH AND HUMAN SERVICES
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20205

June 14, 1984

An Unexpected Water Saturation

Dear Barry,

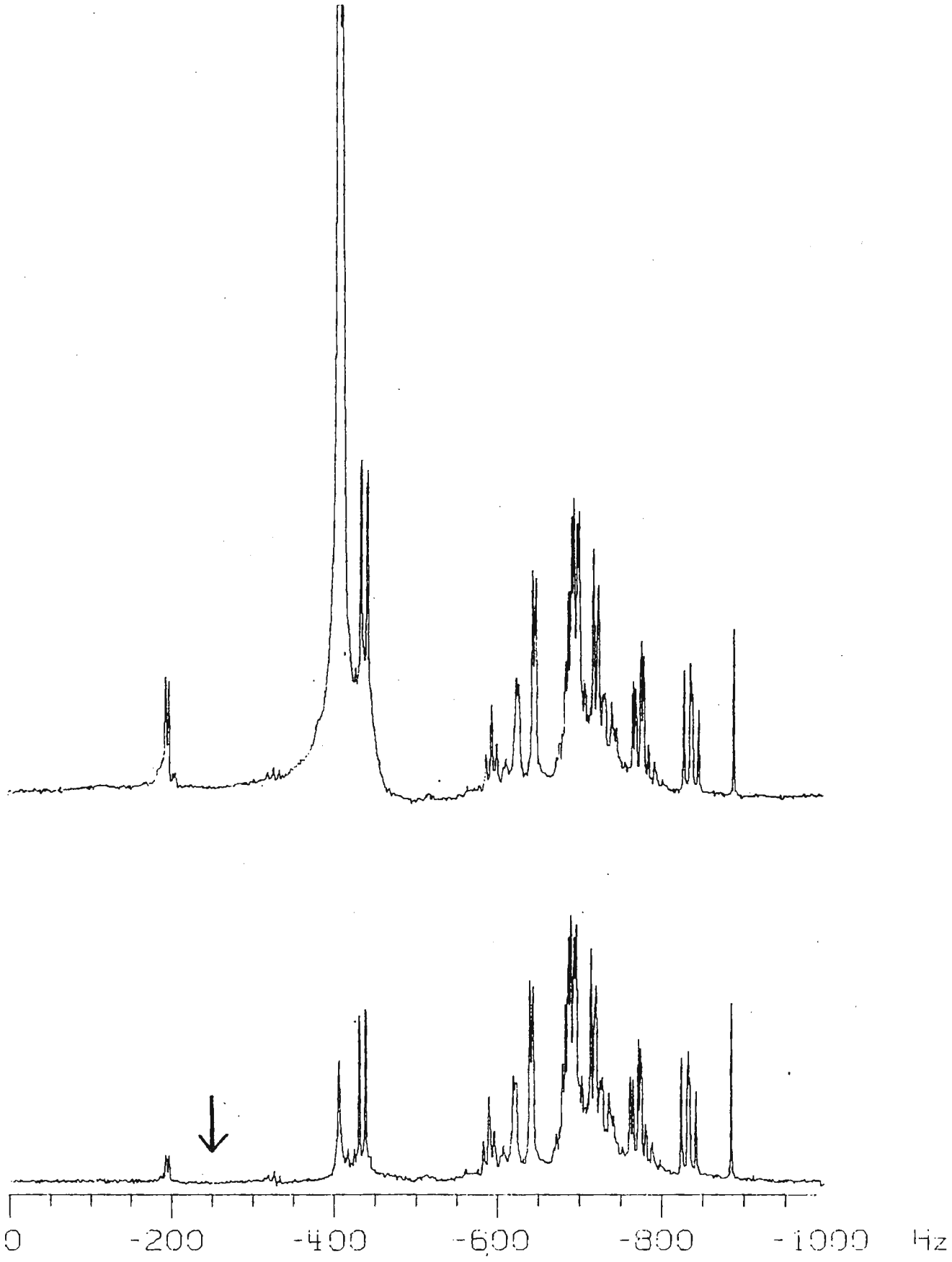
In the course of examining the rates of anomerization of a series of monosaccharides, we came upon an interesting (but I suppose not altogether unexpected) phenomenon. We were in the process of comparing results obtained from two-dimensional NMR with those from the standard saturation transfer of magnetization. One of the molecules we were investigating was galactose-6-phosphate, where we have been interested in the machanizm of anomerization and the role of the phosphate group. In one saturation transfer experiment we were irradiating the C-1 proton of the alpha anomer (see figure) which is found at the lowest magnetic field, and measuring the steady state transfer of magnetization to the C-1 proton of the beta anomer, whose resonance is partially overlapped by the residual water peak. The experiment is carried out by presaturation of the desired resonance for about ten seconds, turing off the irradiating rf field, and then applying a non-selective pulse and recording the FID. When we first carried out the experiment we were somewhat surprised to see the residual water peak reduced considerably in amplitude. To demonstrate the effect more clearly we irradiated at a point 50 Hz upfield from the C-1 proton resonance and about 350 Hz (at 360 MHz) downfield from the water peak as shown by the arrow in the figure. I assume this effect is a result of homogeneous broadening of the residual water resonance by exchange with the labile OH groups on the sugar. Irradiating at other frequencies further from the water resonance does decrease the magnitude of the effect.

Please credit this contribution to Bob Highet, whose desk has taken on the appearance of a rainbow.

Yours very truly,

James A. Ferretti

James A. Ferretti


0
-200
-400
-600
-800
-1000
Hz

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Professor B.L. SHAPIRO
Dpt of Chemistry
Texas A & M University
College Station

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Téléphone : (7) 851.51.51
Télex : ATO 310990

N/Réf. : JJB/CO

V/Réf. :

PIERRE-BÉNITE, le June 14th, 1984

Dear Professor Shapiro,

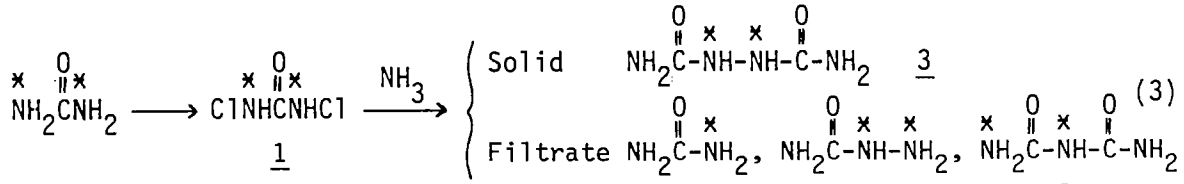
^{15}N-NMR and mechanism of N-N bond formation via N-chloroureas

With our continuing interest in the chemistry of hydrazine derivatives, we have recently been reinvestigating the reaction between chloroureas with ammonia (1) (2). Because of the poor stability of N-chloro-compounds 1 and 2, and the lack of solubility of derivative 3 (< .2 % in water), the reactions were studied by using ^{15}N-NMR from starting ^{15}N-enriched urea (50 % ^{15}N on each site).

N,N'- Dichlorourea 1, prepared by bubbling chlorine at - 5°C into an aqueous solution of urea in the presence of ZnO, gave spectrum A with only one signal at δ 68.84 during the first ten minutes of observation. This compound suffered decomposition and a mixture of 1, N-monochlorourea 2 and urea chlorhydrate was obtained with longer accumulation. Spectrum B described the reaction without ZnO : it was essentially a mixture of N-mono-chloro urea 2 and urea chlorhydrate.

When labeled 1 was treated with aqueous unlabeled ammonia, hydrazodicarbonamide 3, *N-*N labeled, was isolated (spectrum C). Mass spectral data confirmed that 3 was doubly labeled. The analysis of the filtrate (spectrum D) showed essentially urea (half labeled compared to the starting material), labeled semicarbazine 4, biuret 5 and unidentified species at δ 142.35.

The distribution of ^{15}N summarized below, showed the usefulness of ^{15}N-NMR as tracer determination of N-N bond formation.



(3)

*N = labeled ^{15}N

.../...

(1) F.D. Chattaway J. Chem. Soc. 95, 235 (1909)
(2) C.S. Grove Jr, G.F. Grillot, R.C. Chang J. Org. Chem. 1961, 26, 4131.
(3) Labeling pattern unknown for 4, 5.

M. DUBOEUF R. MARAVAL P. TELLIER J.J. BARIEUX

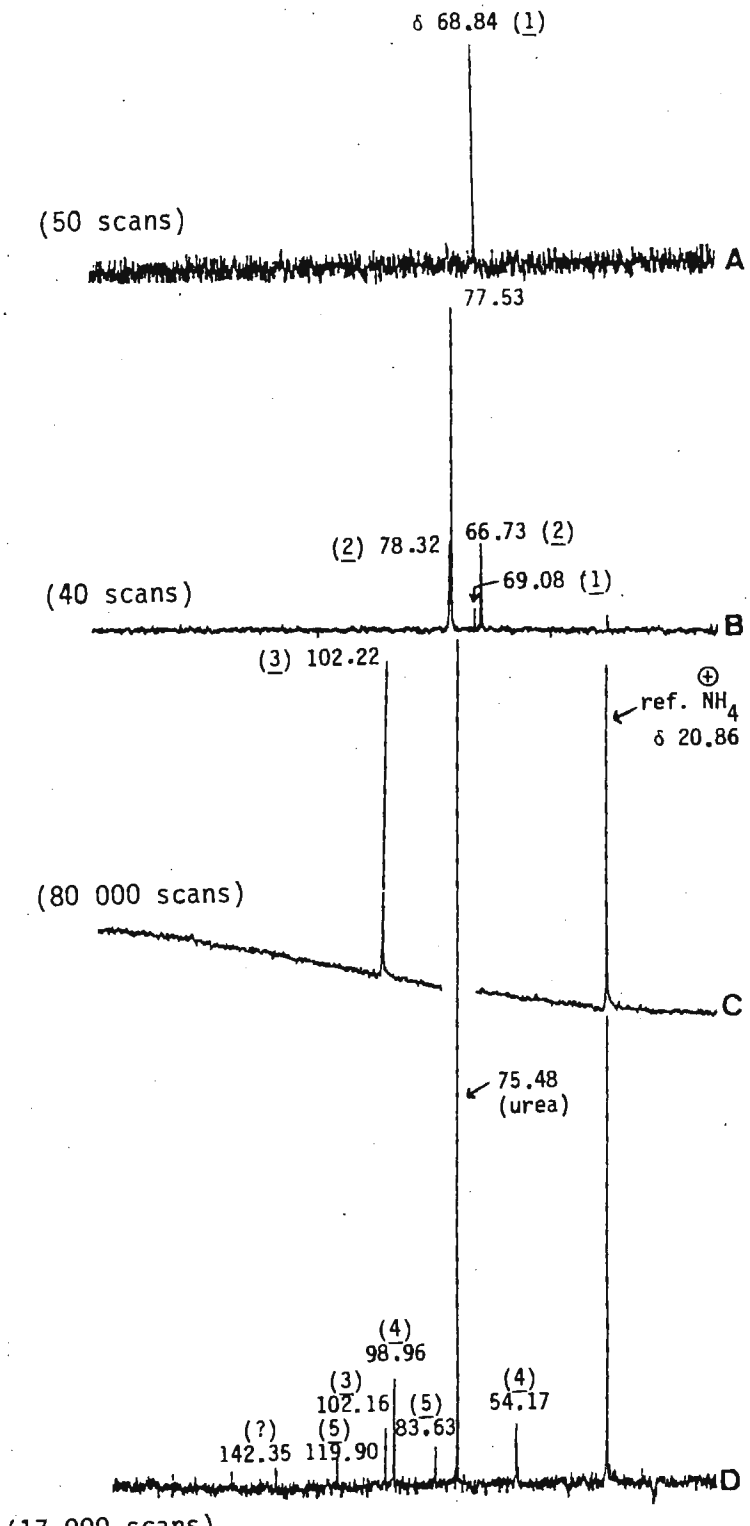


FIG. ^{15}N-NMR (20.18 MHz)

1 ClNH-C(=O)-NHCl

2 ClNH-C(=O)-NH_2

3 NH_2C(=O)-NHNH-C(=O)-NH_2

4 NH_2C(=O)-NH-NH_2

5 $NH_2(C(=O)-NH)_2$-H

(δ derived value from liquid ammonia)

THE UNIVERSITY OF NEW ENGLAND
ARMIDALE, N.S.W. 2351.

Professor B.L. Shapiro,
Department of Chemistry,
Texas A. & M. University,
COLLEGE STATION, Texas 77843-3255,
U.S.A.

13th June, 1984.

Dear Barry,

CONFORMATION OF BUTYROLACTONES REVISITED

Everybody is revisiting these days.....Five years ago [Newsletter, 245-48], I wrote that ab initio calculations on the geometry of butyrolactones gave dihedral angles in good agreement with deductions (1) made from values of proton-proton coupling constants.

Those calculations assumed, on the basis of earlier X-ray crystallographic results, that butyrolactones favoured an 'envelope' conformation and, in order to keep computation time within reasonable limits, also made a number of simplifying assumptions then regarded as normal. Since then, there have been substantial improvements in computer hardware and software, and it is becoming routine to tackle molecules of the size of butyrolactone with a minimum of assumptions.

Such a study last year, during a period of Study Leave at the Australian National University, showed that the twisted-ring, 'half-chair', conformation of butyrolactone itself, with an angle between the O-C1-C2 plane and the C3-C4 bond of 18.7°, is lower in energy than the planar conformation though by only 4.5 kJ/mol.

More interesting is the case of 3-hydroxybutyrolactone. Its energy in the twisted-ring conformation [with an angle, as just defined, of 22.0°] is lower than that of the envelope conformation [with the flap bent 7.6° out of the CCOC plane], but by only 0.3 kJ/mol. A 5° twist either way costs only 3-4 kJ/mol, but bending the flap up or down is a much more costly process. In either conformation, the 3-hydroxyl group prefers the [pseudo]-axial position and corresponding vicinal proton-proton dihedral angles (notably, trans: 87.6 ± 1.8°) agree within 2.5°. For the two conformations, INDO-calculated coupling constants are the same within 0.2 Hz, and in reasonable agreement with experimental values (1); agreement is, however, very poor if the ring is twisted 5° in either direction from the optimized geometry, but the average values still agree. N.m.r. methods are, of course, insensitive to the small twisting energies involved, but did get the axial location of the OH group and the average trans dihedral angles (ca 90°) right!

Yours sincerely,

Noel Riggs

N.V. Riggs,
Professor of Organic Chemistry.

(1) Tetrahedron Lett., 1967, 5113.

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June 22, 1984

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

^{1}H-NMR of Peptides in Reverse Micelles

Dear Prof. Shapiro:

after having played for a while with opioid peptides in the presence of $C_{12}PN$ (1) and SDS (2) normal micelles in water solution, we felt tempted to investigate a little more sophisticated system. The figure shows variable temperature spectra of Met-Enkephalin in the presence of AOT reverse micelles in isooctane solution. Approximately 1 mg of peptide in 5 µl H_2O was shaken with 0.3 ml of Aerosol OT 50 mM in isooctane (protonated), until the solution became perfectly clear (3). The signal for the deuterium lock was provided by a capillary containing DMSO-d_6. Spectra were acquired in single channel detection with a Bruker HX-270 spectrometer, using a sweep width of 2700 Hz and a filter width of 1700 Hz, in order to improve the dynamic range. For the same reason, H_2O and isooctane CH_3 resonances were irradiated between scans.

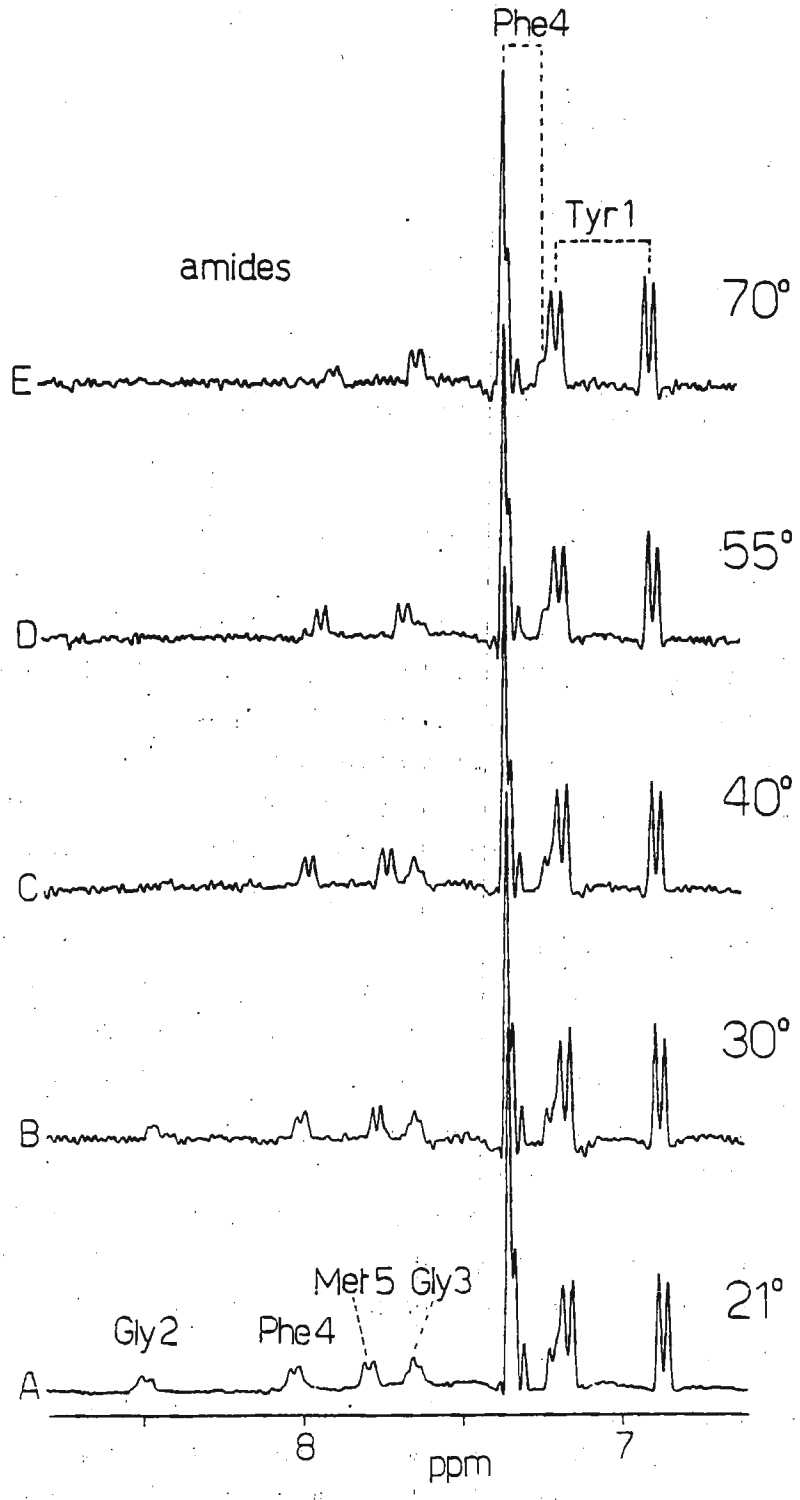
The temperature coefficients of the amide protons, compared with those obtained in water, in DMSO, and in water solution of SDS normal micelles, suggest that in the water pools inside the AOT reverse micelles Met-Enkephalin is more compact than in any of the other systems.

(1) L.Zetta, P.J.Hore and R.Kaptein (1983)Eur.J.Biochem.134,371.
(2) L.Zetta and R.Kaptein, submitted for publication.
(3) F.J.Bonner, R.Wolf and P.L.Luisi (1980) J.Solid-Phase Biochem. 5, 255.

Sincerely,

Antonio De Marco

Lucia Zetta



Variable temperature ^{1}H-NMR spectra of Met-Enkephalin (Tyr-Gly-Gly-Phe-Met) in AOT/isooctane/H_2O reverse micelles.

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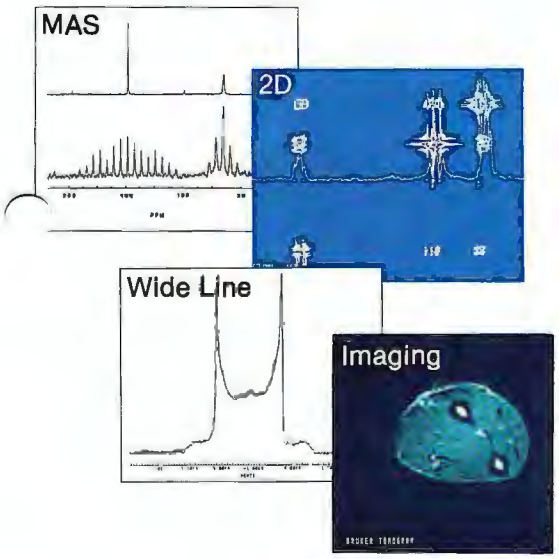

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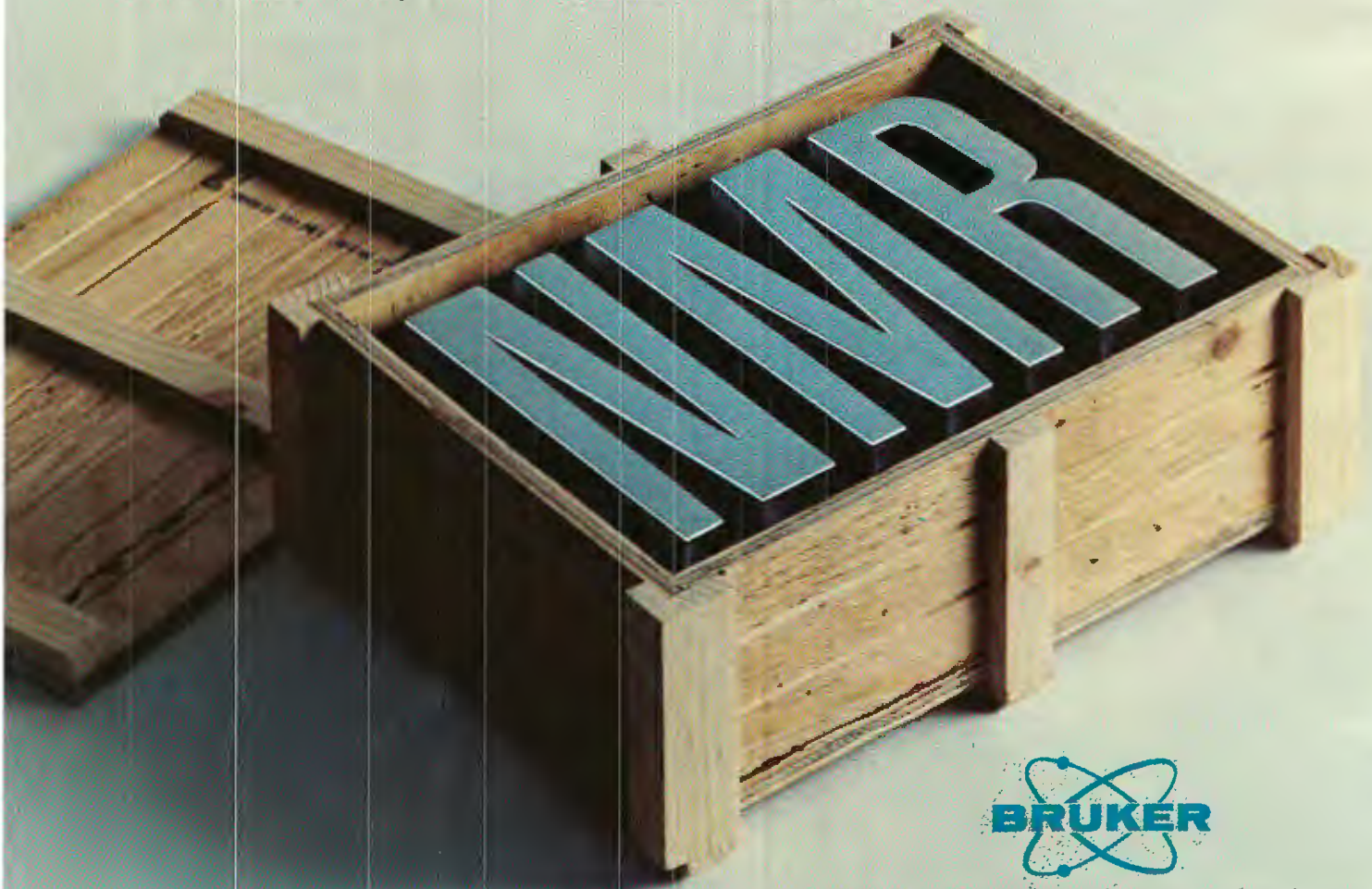

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June 14, 1984

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

Dear Dr. Shapiro:

Re: In Vivo ^{31}P NMR of Corn Earworms

^{31}P NMR has become a widespread technique for studying living tissues and organisms.[1] In particular, single organisms can be studied in vivo at the molecular level. The top figure shows a typical ^{31}P spectrum of an intact corn earworm (Heliothis Zea) obtained with a Bruker WM 360 spectrometer. The spectrum is referenced to an external 85% H_3PO_4 standard.

We have had an interest in physically, rather than chemically, restraining the motion of the corn earworm while acquiring data. For this purpose, a special NMR tube, as shown in the bottom figure, was constructed from Delrin plastic. The small hollow portion of the upper tube provides air to the earworm, which is housed in the lower sample cavity. The pieces simply press fit together, bypassing the difficulty of sliding the earworm past screw threads. The bottom cap can be removed to allow easy cleaning of excreted material from the worm.

Please credit this to Charlie Reilly's account.

Sincerely,

Bob Taylor J. A. Ferris G. E. Pollard/RET

R. E. Taylor J. A. Ferris G. E. Pollard
Analytical Chemistry Department

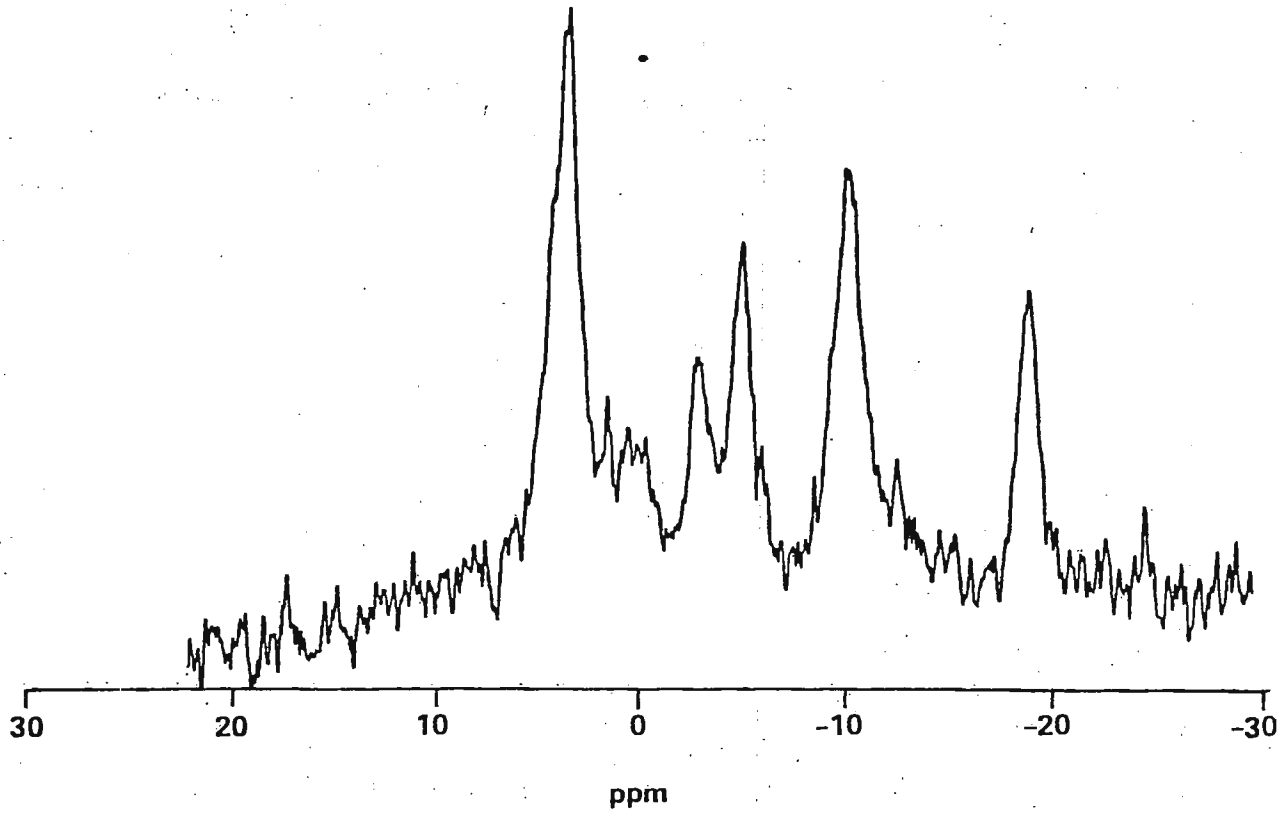
RET/saj

Attachment

cc: T. B. Malloy
C. A. Reilly

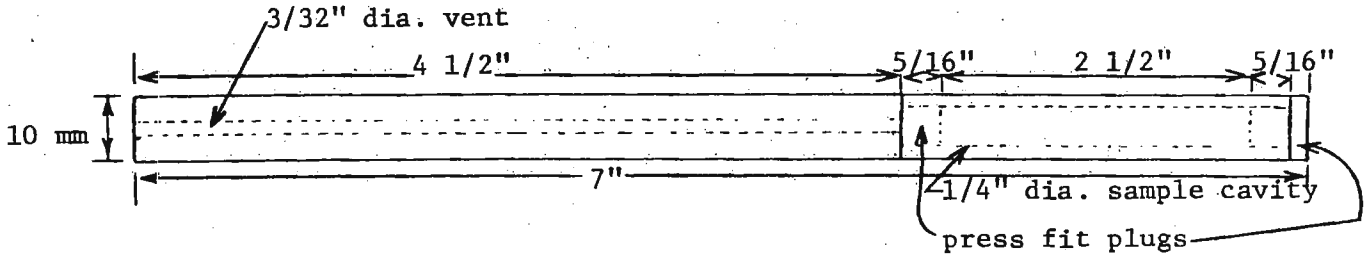
1) R. A. Iles, A. N. Stevens, and J. R. Griffiths, Prog. NMR Spec. 15, 49 (1982).

IN VIVO ^{31}P NMR SPECTRUM OF A CORN EAR WORM



UPPER TUBE

SAMPLE CHAMBER



DELRIN SAMPLE TUBE

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

June 14, 1984

Homonuclear 2D experiments in paramagnetic hemeproteins: ferricytochrome c

Dear Barry,

This contribution is to reinstate our subscription to the TAMUNMR newsletter.

We have now spent several months assessing the utility of 2D NMR methods to aid in our problems with signal assignments in hemoproteins, particularly when paramagnetic. Our initial results are very promising, as two 2D experiments not only confirmed all known [1] steady state NOEs in ferricytochrome c, but also allowed the determination of their spin multiplet connectivities.

Shown in the Figure is a combination plot of NOESY/COSY spectra of a 15 mM ferricytochrome c solution in D_2O. In the NOESY spectrum (upper left), there are through-space (but not through-bond) connectivities between spins a,d and a,g (the a,g cross peak is small but 100% reproducible). There is also a strong NOE between protons d and g. The two single protons (peaks d,g) are bond-coupled, as seen in the off diagonal COSY peak. Since peak a arises from the heme 8-CH_3, d,g must be the geminal protons of the α-methylene group of the adjacent 7-propionate group. Similarly useful data on space and bond connectivities can be seen for a large number of signals. A detailed analysis is in progress. However, we are quite optimistic about the utility of 2D methods in paramagnetic proteins in spite of the short relaxation times and exceptionally large bandwidths.

The homonuclear 2D experiments (both COSY & NOESY) were recorded on our Nicolet 500 spectrometer equipped with a 293 C pulse programmer and a 1280 computer. The solvent peak (HOD) was supressed by constant irradiation. To eliminate the "J-cross" peaks in the NOESY spectra, a composite 180° pulse in the mixing period (100 ms) was inserted[2]. Data were collected as a 128 x 512 (real part) matrix, zero-filled twice along the F1 dimension to make the square set (512 x 512) for symmetrization. Quad detection & sine bell digital filtering were executed in both dimensions. Five contours have been plotted and the conventional 1-D spectrum (with labels a - y) is shown at the top.

Sincerely yours,

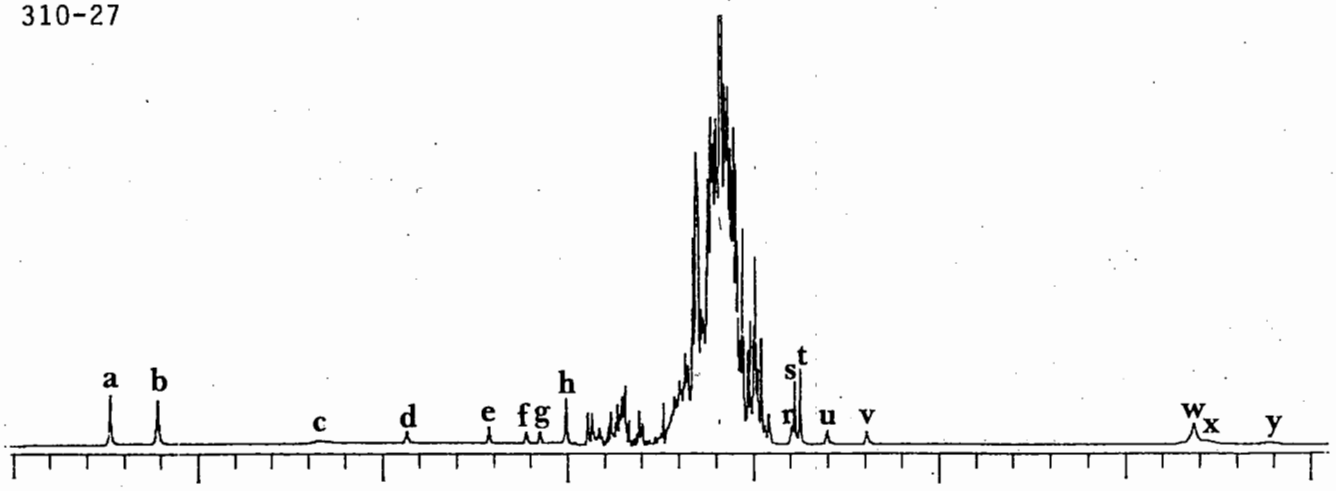
Gerd

Gerd N. La Mar
Professor of Chemistry

Chin Yu

Chin Yu
Postdoctoral Associate

1. S. McLachlan, S. Ramaprasad, & G.N. La Mar, unpublished results.
2. S. Macura, K. Wuthrich & R. Ernst, JMR, 47, 351 (1982).



NOESY
FERRIC CYT. C

COSY
FERRIC CYT.C

40 30 20 10 0 -10 -20 -30 PPM

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Improved SPT

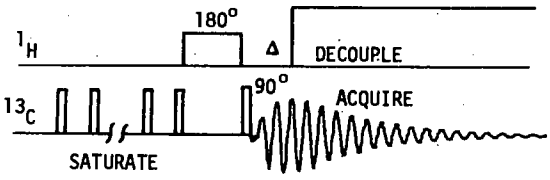
Dr. Bernard L. Shapiro
TAMU NMR Newsletter
Department of Chemistry
Texas A&M University
College Station, Texas 77843

June 8, 1984

Dear Barry:

During the past several years, an enormous number of increasingly complicated new one- and two-dimensional NMR experiments has been proposed in the literature. Against suggestions made in the advertisement world, we believe that "newer" does not always mean "better."

We found that the old selective population transfer (SPT) experiment (1) can be used very conveniently for the one-dimensional correlation of ^{1}H and ^{13}C chemical shifts. The major modification we made to the SPT experiment is to switch on the ^{1}H decoupler a time, $\Delta=1/2J$ (or $1/4J$ for CH_2 and CH_3), after the 90° ^{13}C observe pulse, whereas data acquisition is started immediately after the 90° pulse. ^{13}C presaturation is also used. It can easily be shown that the observed decoupled SPT



signal will be +90° or -90° out of phase with respect to resonances in a regular (NOE-enhanced) FID spectrum, depending on whether the high-field or the low-field satellite in the ^{1}H spectrum has been inverted by the selective 180° pulse. Therefore, no ambiguity remains about whether the signal is due to transfer from the high-field satellite of one proton or from the low-field satellite of another.

For optimum sensitivity one wishes to invert the entire ^{13}C satellite, which is broadened by homonuclear ^{1}H coupling. Therefore, one wants to use a rather strong rf field for the selective ^{1}H pulse. This would lead to poor selectivity in the ^{1}H spectrum. In practice, a proton rf field strength of approximately 20 Hz turns out to be a good compromise, giving efficient spin inversion and still good selectivity.

Figure 1 shows an example of the technique applied to a 16 mM solution of chrysene, a potent carcinogen, in $CDCl_3$. Spectra are recorded on a Nicolet NT-500 spectrometer. All signals transferred from low-field satellites have positive intensity whereas transfer from high-field satellites results in negative intensity. The selective 180° pulse was applied 80 Hz ($J_{CH}/2$) downfield from the various proton chemical shifts. In order to distinguish between C4 and C5, the ^{1}H pulse was applied 85 Hz downfield of proton H5. Even while H4 and H5 are separated by only 0.016 ppm, C4 and C5 are easily distinguished.

(1) K. G. R. Pachler and P. L. Wessels, J. Magn. Reson. 12, 373 (1973).

This experiment seems student-proof since there is no phase-cycling that can go wrong and pulse flip angles are not very critical. The experiment is sensitive and easily set up on any spectrometer that has a programmable pulse programmer and the option to change decoupler power under computer control. (If decoupler power is changed by means of a relay switch, an additional 20 msec may be inserted between the 180° ^{1}H pulse and the 90° observe pulse.) No 2D transform and only little data storage space is needed, and therefore this simple experiment is competitive with 2D heteroshift correlation in cases where only a limited number (<10) of resonances have to be correlated.

Kindest regards,

Ad

Susanta

Ad Bax Susanta Sarkar
Laboratory of Chemical Physics

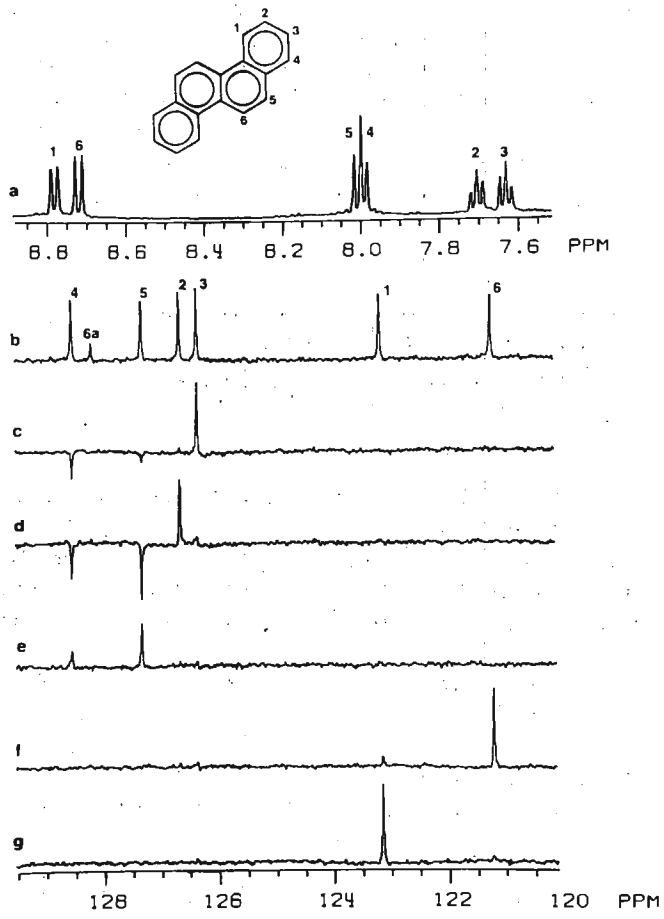


Figure 1: (a) ^{1}H spectrum of chrysene recorded through the decoupler coil of a 10 mm ^{13}C probe. (b) Conventional ^{13}C spectrum (with NOE) obtained in 12 min. (c)-(g) SPT spectra obtained by transfer from the low-field ^{13}C satellites of H3 , H2, H5, H6 and H1, respectively. Negative signals in those spectra result from SPT transfer of the high-field satellites of H4 and H5 which are affected by the soft 180° pulses applied to the down-field satellites of H3 and H2. Each SPT spectrum is the result of 160 scans (10 min.).

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THE UNIVERSITY OF WYOMING

LARAMIE, WYOMING 82071-3838

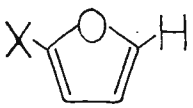
May 31, 1984

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

Title: The ^{17}O NMR Spectra of Substituted Furans

Dear Barry,

In conjunction with our interest in the singlet oxygenation of 2- and 2,5-disubstituted furans we have recently measured the ^{17}O chemical shifts of several of these interesting substrates 1 and 2.



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2

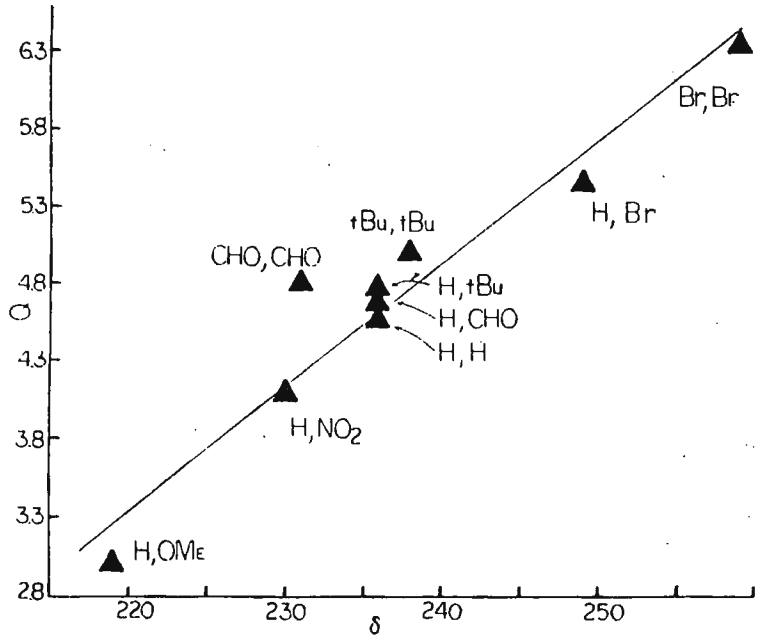
These data were collected on a JEOL FX270 MHz instrument at 36.54 MHz. A total of 4,096 points were collected over a spectral width of 30,030 Hz, utilizing a pluse delay of 50 ms. Sensitivity enhancement was utilized to improve the signal to noise and was accompanied by a 50 Hz artificial broadening of the ^{17}O peaks. These data are reported in the following table.

Table. ^{17}O NMR Chemical Shifts of 2-Substituted and 2,5-Disubstituted Furans.[a]

Compound	δ vs H_2O (width in Hz)	Compound	δ vs H_2O (width in Hz)
X=H;Y=OMe	219(71)	X=H;Y=tBu	236(95)
X=H;Y=NO_2	230(100)	X=Y=tBu	238(51)
X=Y=H	236(58)	X=Y=CHO	231(102)
X=H;Y=CHO	236(85)	X=H;Y=Br	249(86)
		X=Y=Br	259(137)

[a] All ^{17}O NMR's were taken in $CHCl_2$ and referenced to external H_2O by substitution.

The inability to correlate these chemical shifts with Hammett like substituent constants is reminiscent of attempts to rationalize ortho chemical shifts in aromatic systems. Schaefer and coworkers[1] suggested that the ortho effect was due to mixing of excited electronic states of the substituent to the observed nuclei. To rationalize these ortho chemical shifts Schaefer introduced a parameter Q. Indeed Q does correlate to the furan ^{17}O shifts as shown in the following plot.



These results and those for other furans will be submitted for publication in the near future. Please credit this contribution to Dr. Dan Netzel.

Best regards,

M. E. Mehrsheikh-Mohammadi

Edward L. Clennan
Department of Chemistry
University of Wyoming

sl

310-33

UNIVERSITY AT BUFFALO
STATE UNIVERSITY OF NEW YORK

Department of Biochemistry
Schools of Medicine and Dentistry
Faculty of Health Sciences
102 Cary Hall
Buffalo, New York 14214
(716) 831-2727

June 26, 1984

Dr. Bernard L. Shapiro
Editor
TAMU NMR Newsletter
Texas A & M University
Department of Chemistry
College Station, Texas 77843-3255

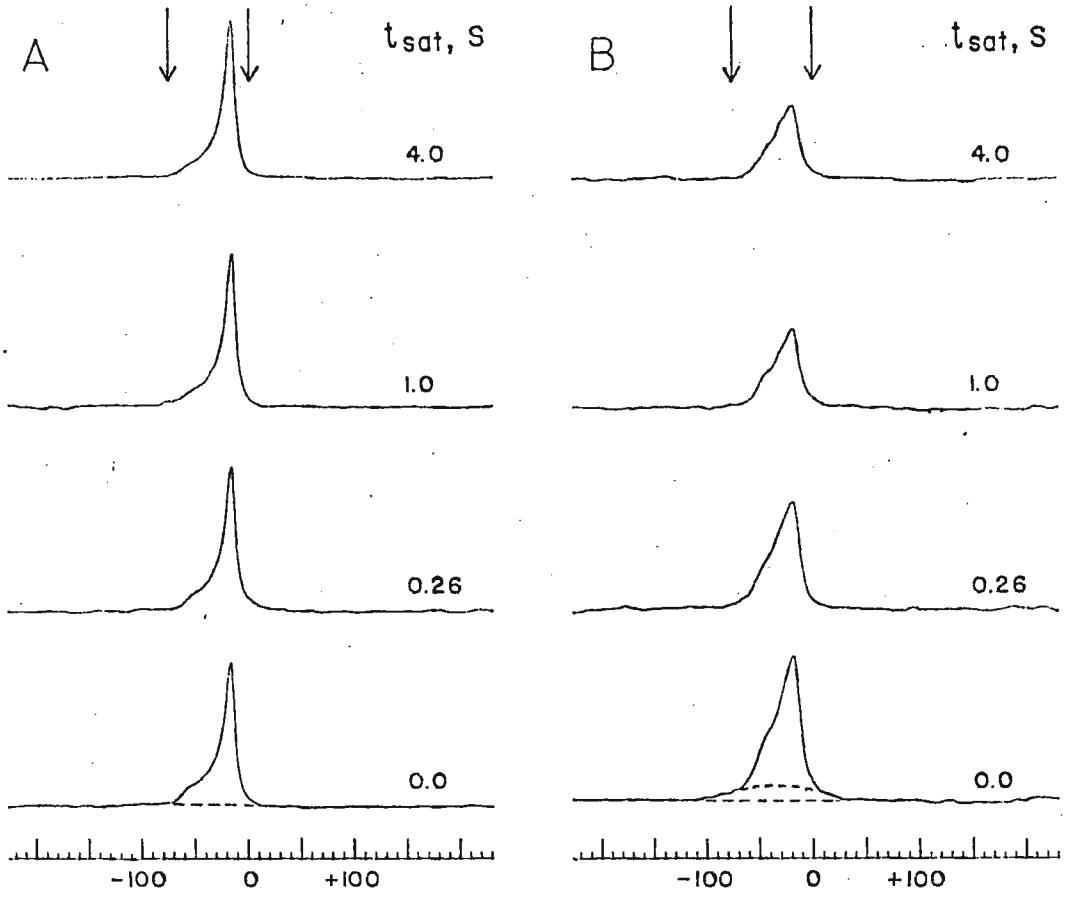
Title: Phospholipid exchange between domains in biological membranes

Dear Dr. Shapiro:

Recently (Biochemistry 23, 2281, 1984) we reported that two different phospholipid domains could be observed in a biological membrane using P-31 NMR. The membrane was the sarcoplasmic reticulum. Using Hahn echo techniques, it was possible to detect a broad component, in addition to the normal P-31 bilayer type resonance in the presence of the calcium pump protein, Ca ATPase. Now we have measured the rate at which phospholipids exchange between the two domains by transfer of magnetization. To do so, we wrote a pulse sequence (with the assistance of Dr. A. Evans of JEOL) to run on our JEOL FX270 which combined the DANTE sequence, for presaturation of the resonance from one domain, with the Hahn echo sequence we have been using to obtain undistorted P-31 NMR powder patterns of membranes. As shown in the left side of the figure, applying this sequence to a P-31 NMR spectrum from pure lipids in which there is no broad component caused no effect (since there is no broad component and thus no resonance intensity in the region of the irradiation). However, application of the same experiment under the same conditions to the sarcoplasmic reticulum spectrum (right side of figure) did show transfer of magnetization from the broad component (which we selectively saturated) to the normal bilayer P-31 resonance. The exchange rate, for which this is the first direct measurement, is about 1 sec., or much slower than had been previously hypothesized. The co-author on this work is Dr. B.S. Selinsky.

Sincerely yours,

Dr. Philip L. Yeagle
Associate Professor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-100
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+100

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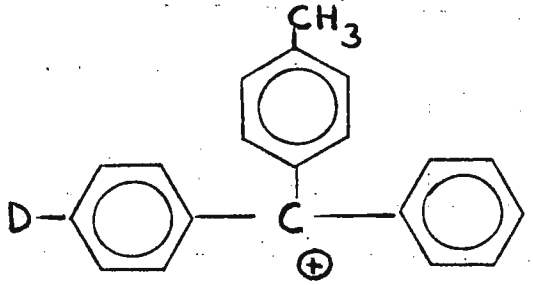
Prof. Dr. B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
USA

^{13}C-NMR Linewidth of Cations

Dear Professor Shapiro,

during the course of our investigations on long range deuterium isotope effects on ^{13}C chemical shifts[1,2] we tried to detect resonance perturbation in 1.



1

Possible isotope effects should be in the order of a few Hz or less. However, we could not get spectra of 1 or similar organic cations of sufficient quality. The linewidth of the ^{13}C-NMR signals was up to 40 Hz on our WH-400 and varied somewhat with the concentration. Even in very diluted solutions of CD_2Cl_2 or CD_3CN the linewidth was not significantly below 10 Hz. Preliminary comparisons with other instruments (XL-100) suggest, that the same solutions give smaller linewidth at lower field, however unacceptable as well. We checked on the obvious suggestion of paramagnetic impurities, but we were unable to obtain an esr signal of the same solutions which shows a radical concentration lower than 10^{-5} mol/l. A survey of the ^{13}C-NMR literature of carbocations reveals that rather seldom a spectrum is reproduced. Most spectra shown in the literature look very broad as well, but the scale to measure the line-

width is not sufficient. Lohman and Maclean[3] have investigated alignment effects on high resolution NMR spectra and found line broadening for quadrupolar nuclei like deuterium, however maintain, that dipolar effects should be very small.
We wonder if somebody of the TAMU-community has made similar observations and could suggest an explanation.

Sincerely yours

Stefan Berger Hermann Künzer

1.) S. Berger and H.Künzer, Tetrahedron 39, 1327-1329 (1983)
2.) S. Berger and H.Künzer, Angewandte Chemie Int. Ed. 22, 321-322 (1983)
3.) J. A. B. Lohman and C. Maclean, Chemical Physics 35 269-274 (1978)

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June 15, 1984

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

Misusing a NMR Spectrometer for Structural Studies of the Universe

Dear Professor Shapiro,

Use of all the known and still to be invented NMR techniques for the study of the structure of matter at the microscopic level (molecules) or their low-entropy conglomerates (organisms) is well known. NMR tomography is a step in the right direction, but does not take one far enough. In order to reach for the ultimate, we decided to use NMR instrumentation for the study of the Universe as a whole. It is well known in astrophysics that only a small fraction of matter is visible while the invisible majority - the missing mass - makes up the most of it. The invisible mass may be neutrino haloes surrounding galaxies and their superclusters, or if neutrinos turn up to be massless after all, then some other kind of inos (gravitinos, squarks, etc.). If the neutrino mass is about 10 eV, then it is enough to constitute most of the invisible mass and to close the Universe as well.

We have changed a Bruker CXP solid state high resolution NMR spectrometer, equipped with a large-bore 4.7 Tesla superconducting magnet, into an ion cyclotron resonance spectrometer and measured with the standard NMR electronics and computer equipment the ion cyclotron resonance (ICR) frequencies of a very small number, a few hundred, of $^3H^+$ and ^3He ions in high vacuum (about 10^{-8} Torr) in the 4.7 Tesla field. At 24 MHz ICR frequency the linewidth is about 0.5 Hz + 0.5 Hz line broadening, but using the DISCXP Lorentzian fit program, line centers can be determined to 10^{-3} Hz, thus creating a mass spectrometer of immense resolving power, better than $1:10^9$. At better than ppb resolution, the ion mass difference could be measured with an error of a few eV and is 18588 eV, or 18599 eV for the atoms.[1] This is quite large and unless β-spectroscopists are greatly in error with their β-decay endpoint energies, the electron neutrino is likely to have a rest mass of up to and about 10 eV, which makes it probably a Majorana particle and closes the Universe. We are not surprised, but are interested in the correlation time of its pulsating dynamics and intend to invent a few other novel uses for our numerous superconducting and digital toys.

With warmest greetings,

E.Lippmaa J.Past J.Puskar R.Pikver E.Suurmaa

1. E.Lippmaa, R.Pikver, J.Past, J.Puskar, E.Suurmaa, I.Koppel, A.Tammik, Pis'ma JETP, 39, (11) 529-531 (1984)

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Dear Dr. Shapiro,

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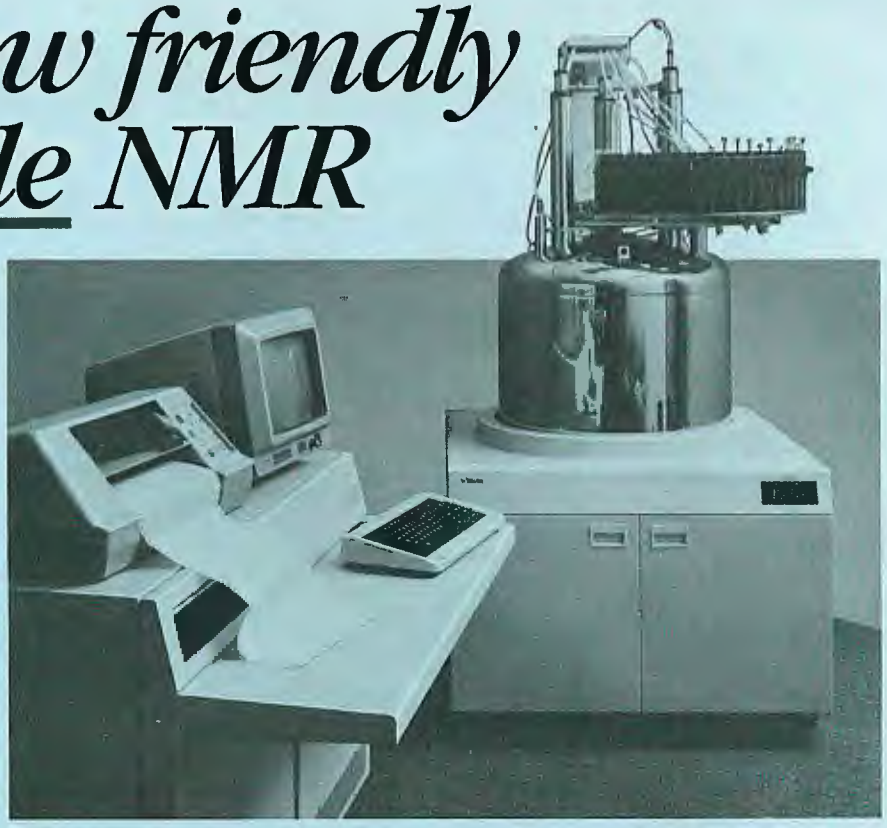
Sincerely yours,

Dennis A. Torchia

Dennis A. Torchia, Ph.D.
Mineralized Tissue Research Branch
National Institute of Dental Research

Find out how friendly and versatile NMR can be.



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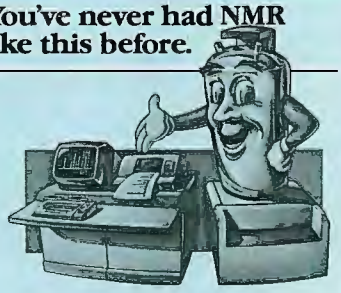

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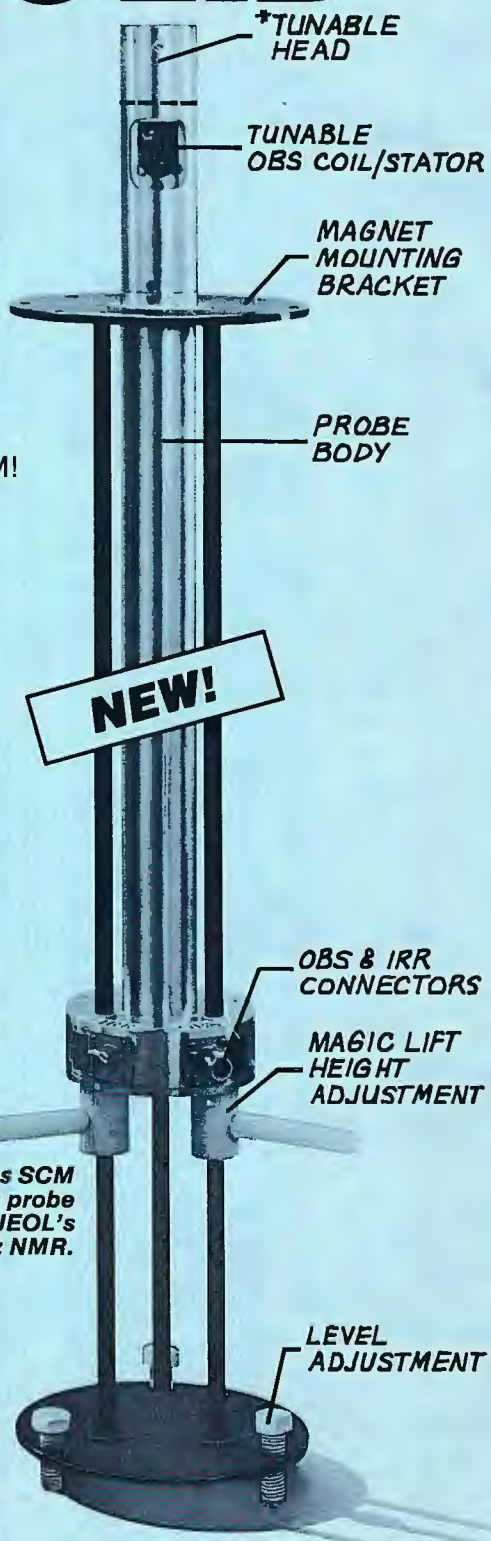

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