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NMR NEWSLETTER

BRIAN SYKES

NO. 329

FEBRUARY 1986

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TEXAS A&M UNIVERSITY

NMR NEWSLETTER

AUTHOR INDEX ---- TAMU NMR NEWSLETTER, NO. 329, FEBRUARY 1986

FORTHCOMING NMR MEETINGS (Additional listings are solicited)

British Radiofrequency Spectroscopy Group - April 9-11, 1986; Oxford University, Oxford OX1 3QR England; see Newsletter No. 323, p. 23.

27th ENC - April 13-17, 1986; Hilton Hotel; Baltimore, Maryland; see Newsletters No. 328, p. 8 and No. 323, p. 31.

8th Rocky Mountain Regional Meeting - June 8-12, 1986; Denver Convention Complex; Denver, Colorado; Meeting Chairman: William E. Beard, USDA-ARS, P.O. Box E, Ft. Collins, Colorado 80522.

4th International Symposium on NMR Spectroscopy - June 16-20, 1986; Tabor, Czechoslovakia; Chairman: Dr. Petr Trska, NMR Laboratory, Institute of Chemical Technology, Suchbatarova 5, CS-166 28 Prague 6, Czechoslovakia.

Scuola Internazionale di Fisica E. Fermi: The Physics of NMR Spectroscopy in Biology and Medicine - June 24-July 4, 1986; Varenna, Italy; Chairman: Professor B. Maraviglia, Dipartimento di Fisica, Universita degli Studi, "La Sapienza," P. le Aldo Moro, I-00185 Roma, Italy.

International Society of Magnetic Resonance (ISMAR), 9th Meeting - June 29-July 5, 1986; Hotel Gloria; Rio de Janeiro, Brazil. Chairman: N.V. Vugman, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil.

U.S.-Latin American Workshop on Recent Developments in Organic and Bioorganic NMR - July 7-11, 1986; Campinas, Brazil; see Newsletter No. 323, p. 59.

28th Rocky Mountain Conference - August 3-7, 1986; Radisson Hotel; Denver, Colorado; Conference Chairman: R. Barkley, CIRES, University of Colorado, Boulder, Colorado 80309, (303) 492-1158. Abstract Deadline: March 21, 1986. NMR Chairmen: J. Haw, Dept. of Chemistry, Texas A&M University, College Station, Texas 77843, (409) 845-1966, and F. Miknis, Western Research Institute, Box 3395, University Station, Laramie, Wyoming 82071, (307) 721-2307.

XXIII Congress Ampere on Magnetic Resonance - September 15-19, 1986; Rome, Italy; XXIII Congress Ampere, Dipartimento di Fisica, Universita de Roma, "La Sapienza," P. le Aldo Moro 5, I-00185 Roma, Italy.

Federation of Analytical Chemistry and Spectroscopy Societies (FACSS XIII) - September 28-October 3, 1986; St. Louis, Missouri; Program Manager: Dr. Sydney Fleming, FACSS (Titles), 24 Crestfield Road, Wilmington, Delaware 19810.

1986 Eastern Analytical Symposium - October 20-24, 1986; Hilton Hotel, New York; see p. 23 and Newsletter No. 325, p. 27.

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.

DEADLINE DATES

No. 331 (April) --------- 28 March 1986

No. 332 (May) ---------- 25 April 1986

UNIVERSITÉ DE LAUSANNE

INSTITUT DE CHIMIE ORGANIQUE

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19 November 1985

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

INEPT in ^{17}O NMR

Dear Professor Shapiro,

^{17}O NMR spectroscopy has undergone a dramatic development in recent years and may now be considered as a routine method[1]. There are, however, almost no experimental methods available to perform an assignment of the spectra. Usually specific enrichment, chemical shift - structure relationships etc. are employed. To overcome this problem we have used the INEPT sequence to distinguish between protonated and non - protonated oxygens. With an average coupling constant $^{1}J(^{17}O, H)$ of 85Hz, the value of 0.0056 J^{-1} for the interpulse delay τ[2] and the addition of 0.01 M $Cr(acac)_3$ to shorten the proton T_1's we obtained good INEPT spectra of simple alcohols (^{17}O in natural abundance) within a few minutes. When trying to determine the coupling constant from the separation of the two INEPT lines it is to be realised that this distance is usually larger than the actual coupling constant. A fitting of the experimental spectrum with two lorentzian lines by a least squares procedure provided the desired results. Fig. 1 shows a typical spectrum. To study further the influence of the linewidth on the apparent coupling constant $\tilde{J}$ in an INEPT spectrum we calculated some spectra. Fig. 2 shows the results and Fig. 3 the functional dependance of $\tilde{J}$ on the linewidth $\Delta\nu_{1/2}$. As a general rule one can say that only for $J > \Delta\nu_{1/2}$ $\tilde{J}$ corresponds to the true coupling constant J.

Sincerely,

Martin Schumacher

P.S. Please credit this contribution to the account of Prof. A. Merbach

1) J. P. Kinzinger in "NMR of Newly Accessible Nuclei", P. Lazlo, Ed., Academic Press, New York, Vol. 2, p. 75 (1983)

2) D. T. Pegg et al., J. Magn. Reson. 44, 32 (1981)

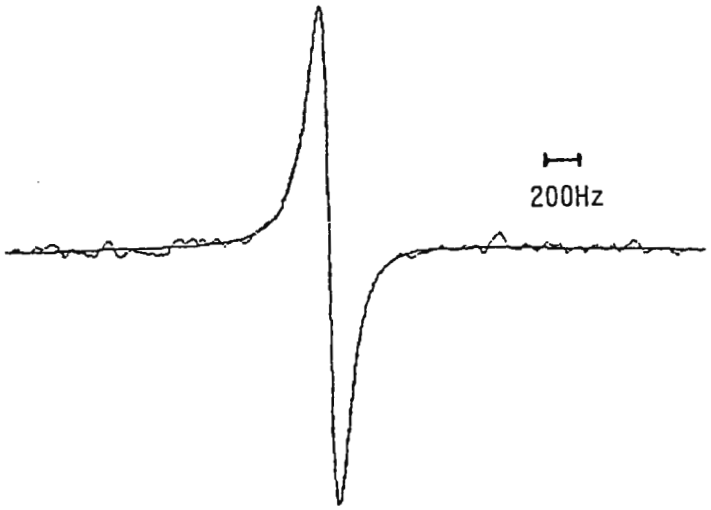

Fig. 1 Experimental ^{17}O NMR spectrum of neat ethanol (LB = 50Hz) with superimposed simulated spectrum

Measured: $\Delta\nu_{1/2}$ = 173Hz, $\tilde{J}$ = 142Hz

Calculated: $\Delta\nu_{1/2}$ = 175Hz, J = 81Hz

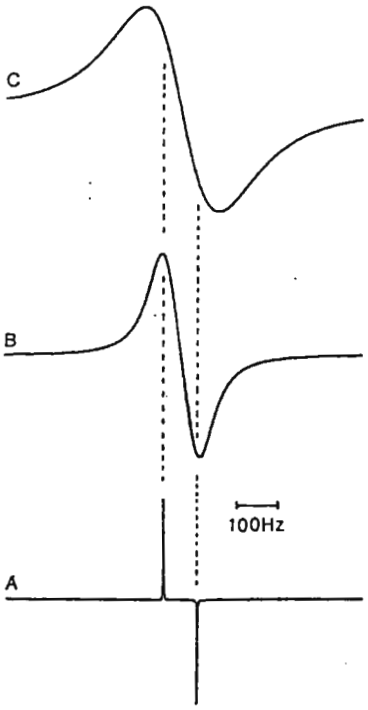

Fig. 2 Calculated INEPT spectra

A $\Delta\nu_{1/2}$ = 1Hz

B $\Delta\nu_{1/2}$ = 100Hz

C $\Delta\nu_{1/2}$ = 300Hz

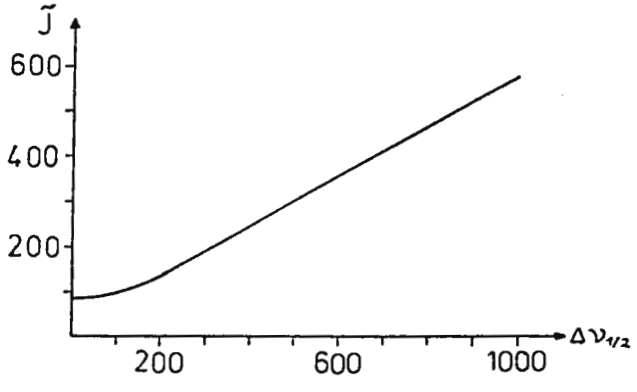

Fig. 3 Dependance of the apparent coupling constant $\tilde{J}$ on the linewith $\Delta\nu_{1/2}$; J = 85Hz

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December 15, 1985

Re: Magic Angle Proton NMR of Natural Mordenites

Dear Prof. Shapiro:

Recently we have been working on natural mordenites using solid state magic angle ^{29}Si, ^{27}Al and ^{1}H NMR techniques.

The MAS proton NMR spectra are shown in Figures a-d for type-Y faujasite, Na-mordenite, natural mordenite, and dealuminated natural mordenite. All these samples were untreated and equilibrated with water.

The line widths of H_2O signal in Figures a-d show some interesting features about the nature of water and one can correlate with their framework structure. The structure of faujasites reveals (1) that ca 50% volume being void, whereas it is ca 30% in mordenties. Normally, H_2O occupy these voids. The line widths in the spectra of faujasite (a) and mordenite (b-d) reflects on the mobility of water. The narrow line signal for faujasite may be attributed to larger pore size in faujasites compared to mordenites. The constraints on the water molecules in smaller pores is reflected as larger line widths for mordenites (b-d). In these spectra, the CSA and dipolar interactions are not completely averaged by MAS. The H_2O signal is narrower in the spectra of dealuminated natural mordenite (d) compared to starting material, natural mordenite (3).

We also investigated heat treated natural mordenites in which water signal disappears and two unresolved peaks appear and their chemical shifts are different than free water. These two peaks are assigned to protons around Si and Al sites (2, 3).

Sincerely,

Ashok

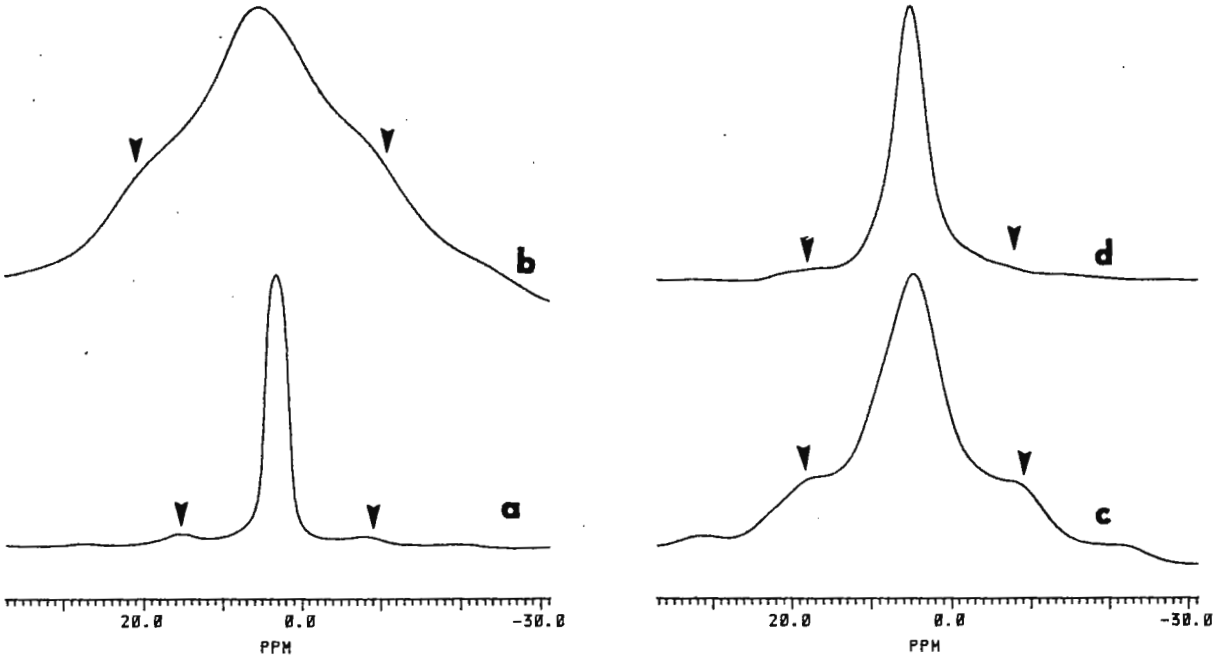
Ashok Cholli

cc: A. Ellgren
AC/jep

1. D.W. Breck, "Zeolite Molecular Sieves", John Wiley & Sons, 1974.

2. K.F.M.G.J. Scholle, W.S. Veeman, J.G Post and J.H.C van Hooff Zeolites 3, 214, 1983.

3. Cholli, A.L., to be published.



January 13, 1986

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

Dear Professor Shapiro:

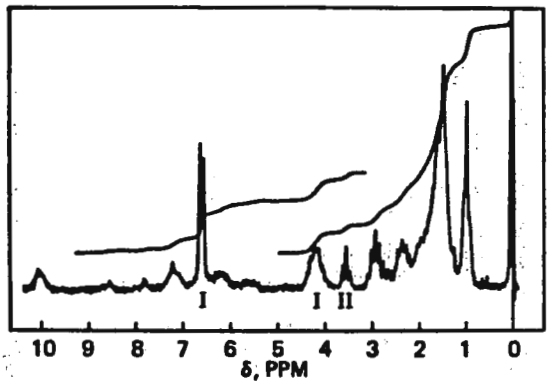
Subject: Quantitation of Aminododecane Isomers by Proton NMR

We have found the use of Lanthanide shift reagents (LSR's) to be very valuable when quantifying two similar isomers of an aminoalkane. During the preparation of 2-aminododecane from 1-dodecene, it became necessary to know the level of the impurity 3-aminododecane.

By using tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium ($Eu(fod)_3$), we were able to quantify the 3-isomer in the presence of the 2-isomer. The figure shown below is a typical proton NMR spectrum containing the LSR and 2-aminododecane (I) in the mole ratio of 0.85 and spiked with 3-aminododecane (II). Representative resonances for each alkane component are marked in the figure. The isomers were quantified using the resonance at 4.2 ppm for I and 3.6 ppm for II.

The lower limit of detection of the 3-isomer was estimated to be 4% at the 10 to 15% 3-isomer level in samples of the 2-isomer and the relative standard deviation was estimated to be ± 10%. No 1-aminododecane was detected by this proton NMR method.

This work was accomplished on a Varian EM-390 NMR spectrometer. The approach of using the shift reagent made it possible to carry out this analysis in a routine manner without requiring the use of a super-conducting magnet. Had a high field NMR been available in the location needing the analysis, it could have been accomplished much better at the higher field strength.



Yours very truly,

Douglas W. Lowman
Senior Research Chemist
Research Laboratories
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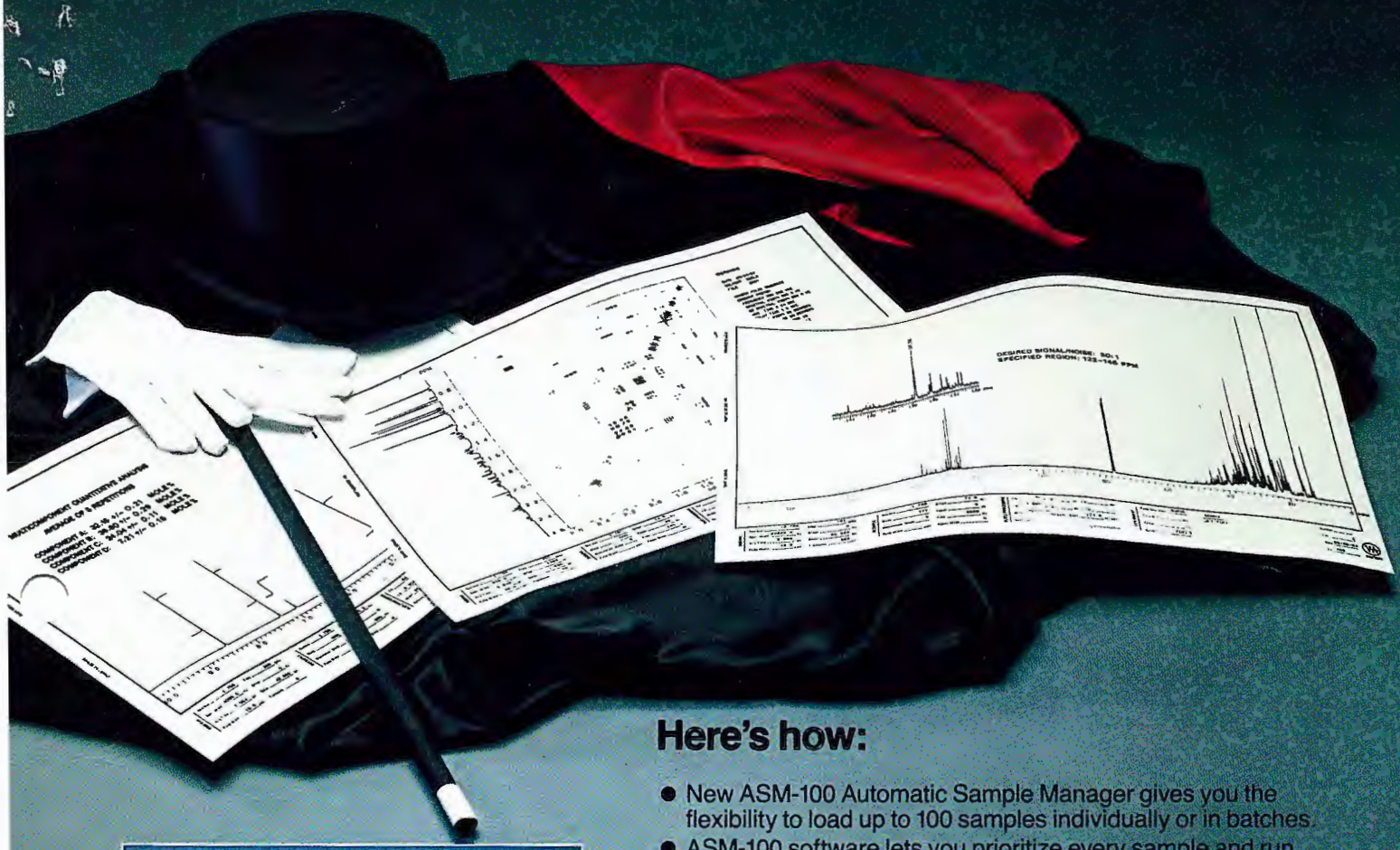

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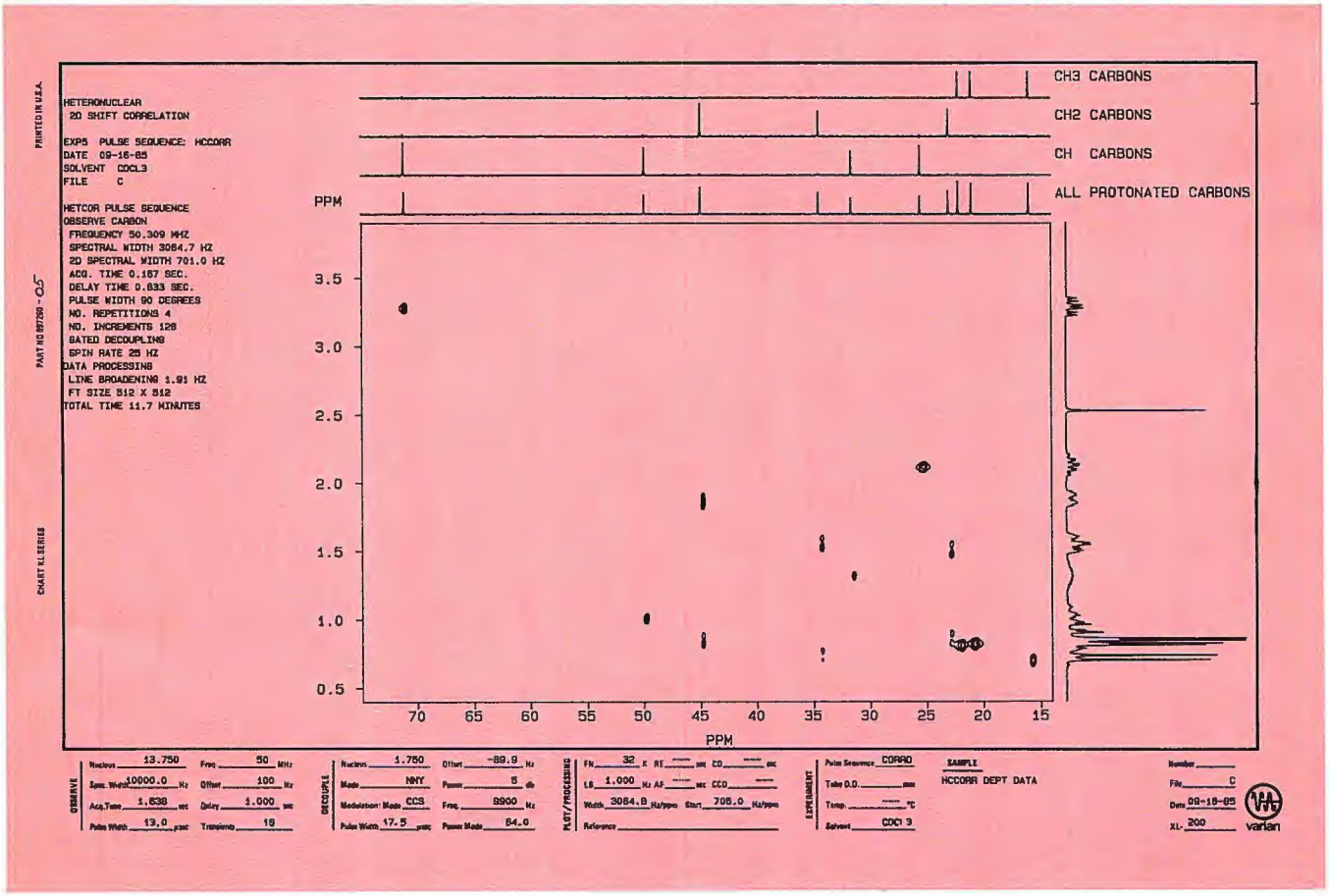

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For the carbon experiment, where sensitivity is more of a problem, the signal-to-noise ratio was checked periodically during the course of the experiment, and the acquisition terminated when a preselected signal-to-noise ratio was reached. Using this number of scans as a guide, conditions were then chosen for the DEPTGL experiment, and that series of spectra was then acquired and automatically combined (spectral editing) to produce subspectra containing, respectively, protonated carbons, CH carbons, CH_2 carbons, and CH_3 carbons.

With 1D spectral information in hand, MAGICAL next determined the minimum spectral width for the heteronuclear correlation experiment for both protons and carbons (using protonated carbons only, as determined from the DEPTGL experiment). The rest of the 2D parameters were also optimized based on the 1D experiments, and the 2D experiment was then acquired, processed, scaled, and plotted. From start to finish, the entire series of experiments required only 22 minutes. This time will, of course, vary from sample to sample, because the MAGICAL analysis is not "canned," but adapts to the requirements of each particular sample.

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CIBA–GEIGY

October 30, 1985

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

Dear Professor Shaprio:

Re: C-13 NMR: Differences in ^{13}C-1 glucose metabolism of Human Red Blood Cells(RBC) in Bicarbonate vs Tris (hydroxymethyl) aminomethane (Tris) Krebs Buffer

Recent ^{13}C NMR studies in our laboratory have shown marked differences in ^{13}C-1 glucose metabolism of RBC in bicarbonate vs Tris Krebs buffer. A number of glycolytic pathway metabolites were observed and identified by ^{13}C NMR spectroscopy in both buffer systems (Figure 1 & 2).

Experimental protocol was as follows. Blood from healthy donors was collected and centrifuged at 1000 x g for 10 min. Plasma was discarded and the cells were washed in ice cold buffer containing 20 - 25 U/ml heparin (3 times). Washed cells were counted in a coulter counter. 10^9 cells were incubated (37°C) with ^{13}C-1 glucose for 30 min with constant oxygenation. The oxygenated cells were introduced into the magnet and spectra were collected on a Varian XL-400 NMR spectrometer. The probe temperature was maintained at 37°C and Waltz decoupling was used to avoid excess heating of the sample.

Our experiments indicate that the rate of C-4 fructose-6-phosphate, 2,3 diphosphoglycerate/3-phosphoglycerate(3-PG) and lactate formation in RBC is enhanced when suspended in Krebs bicarbonate buffer and diminished in Tris Krebs buffer. Likewise, resonances at 70 ppm and 61 ppm corresponding to ^{13}C-4 glucose and ^{13}C-6 glucose respectively, show a greater metabolic flux in the bicarbonate vs Tris buffer.

It should also be noted that a peak appears in the Tris Krebs buffer at 60.8 ppm which is not present in the bicarbonate buffer. This peak corresponds to the methyl group of Tris buffer and should not be mistaken for a glucose metabolite.

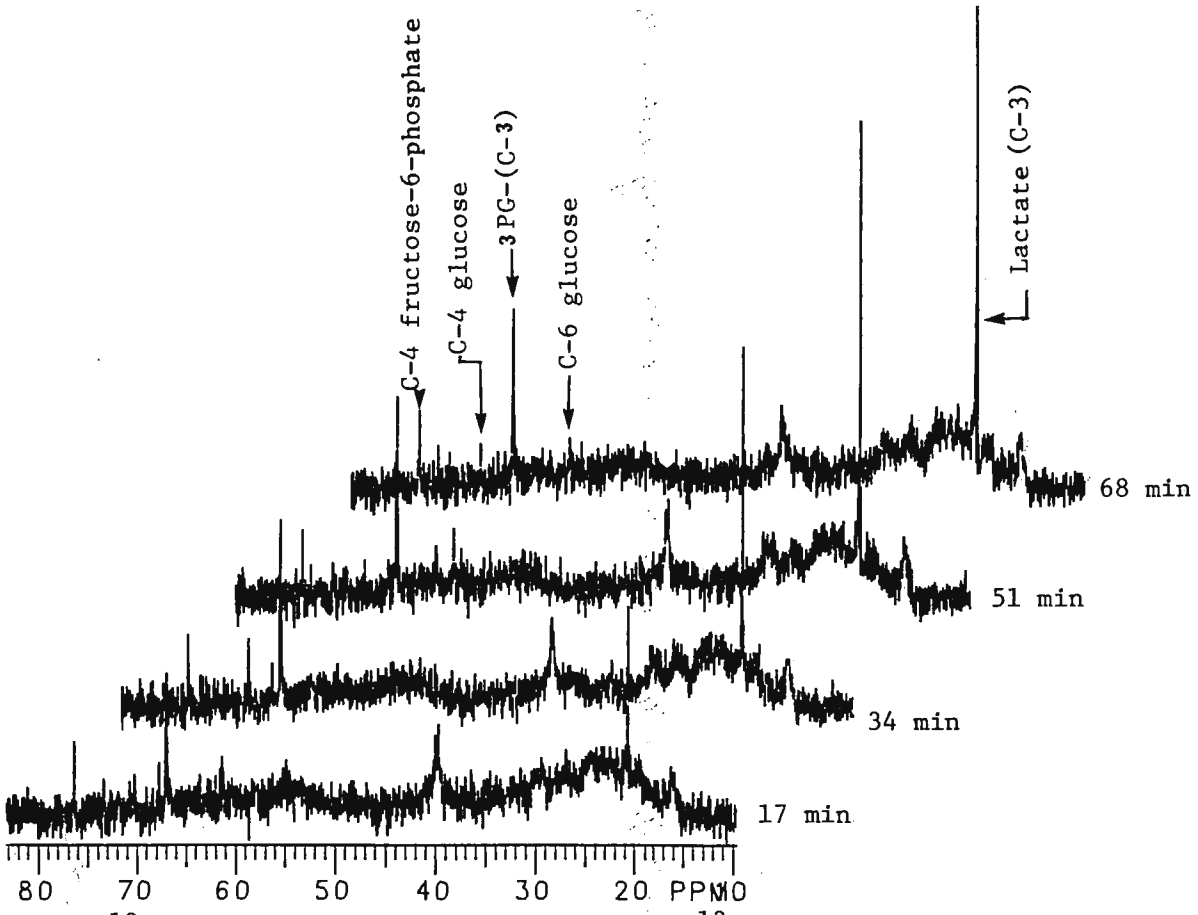

Figure 1. ^{13}C NMR spectra of RBC incubated with ^{13}C-1 glucose in Krebs bicarbonate buffer.

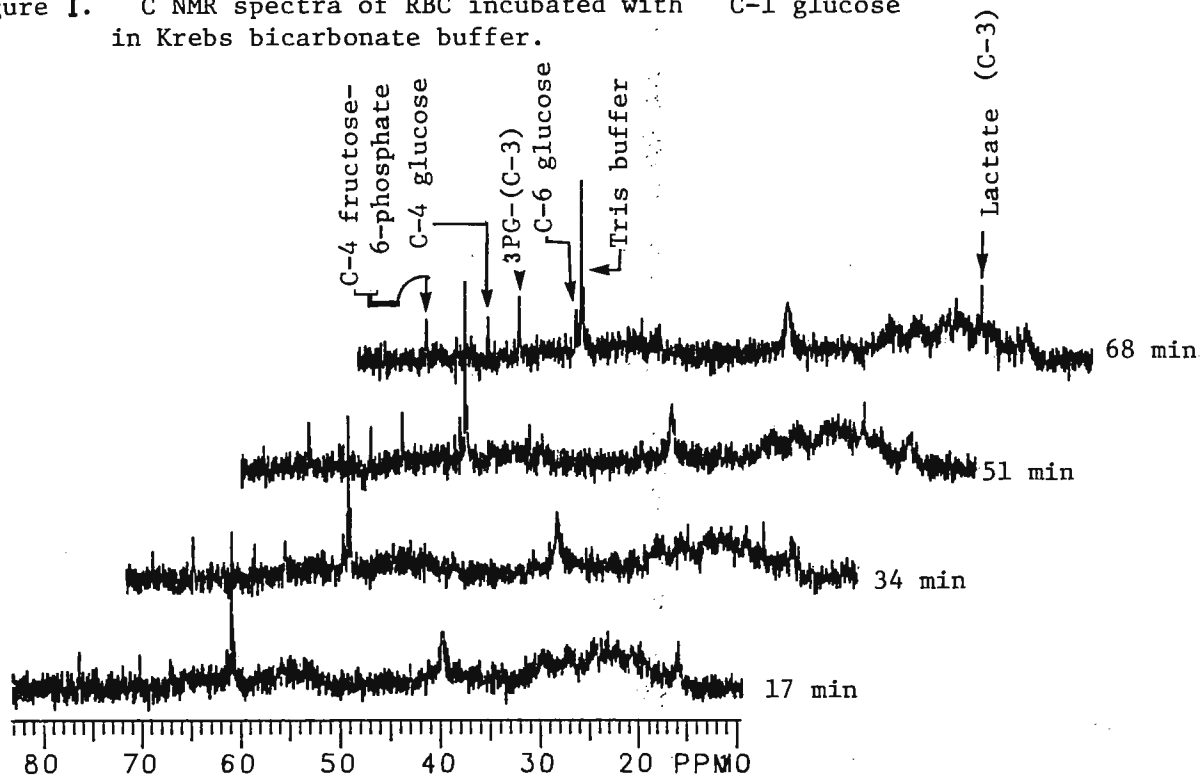

Figure 2. ^{13}C NMR spectra of RBC incubated with ^{13}C-1 glucose in Tris Krebs buffer.

In summary, our data shows that the overall rate of glycolysis in RBC differs when the buffer is the only experimental parameter changed. These results were consistant over several experiments performed in bicarbonate vs Tris buffer, thereby eliminating blood variability as a possible explanation for the observed differences. Finally, this communication serves to stress the importance of maintaining identical conditions when comparing or reproducing biological NMR data.

Sincerely,

Geetha Ghai

Geetha Ghai, Ph.D.

Nina C Gonnella

Nina C. Gonnella, Ph.D.

University of Edinburgh

Department of Chemistry

West Mains Road, Edinburgh, EH9 3JJ Scotland.

Yr. ref.:
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Telex 727442 UNIVED G
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Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station
TEXAS 77843

17 December 1985

Dear Barry,

Comparison of DEPT, APT(GASPE) and SEMUT for carbon multiplicities

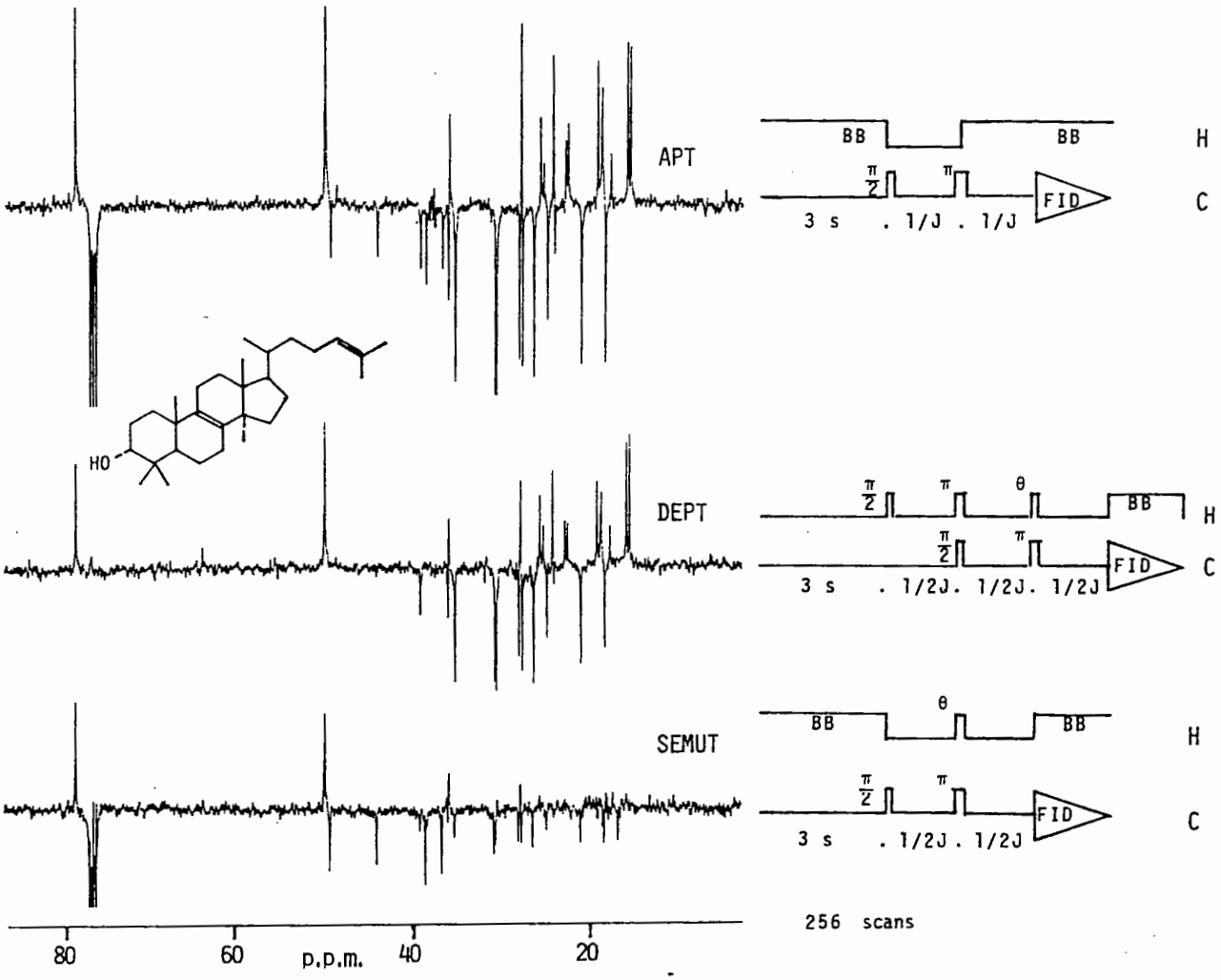
Like many others, we have very successfully used the DEPT[1] pulse sequence to distinguish CH_3 CH_2 and CH resonances and have assumed that this was superior to the other sequences, eg APT(GASPE)[2] and SEMUT[3], which do not involve polarisation transfer. However the 4-fold sensitivity gain of DEPT is not much greater than the 3-fold gain expected with full NOE enhancements in the other sequences. Out of curiousity we decided to compare the three sequences under "identical" conditions, namely those which we have found to give the best signal to noise over a given time for the DEPT sequence.

Using our Bruker WH-360 spectrometer we examined a solution of a tetracyclic triterpene in two probes; a 10 mm multinuclear VSP probe tuned for carbon-13 (90^{o}{C} = 14μs, 90^{o}{Hdec} = 36μs) and a 5 mm selective carbon-13 probe (90^{o}{C} = 8.5μs, 90^{o}{Hdec} = 26μs). A pre-excitation delay of 3 s before the pulse sequence and an acquisition time of 0.5 s were used, the variable pulses being optimised for methylene groups. The results are given in the table along with theoretical intensities assuming full relaxation, complete polarisation transfer in the DEPT sequence and full NOE in the other two sequences. Spectra for the VSP probe are shown. In summary, for the conditions employed, the APT(GASPE) sequence gives rather better signal to noise than the DEPT sequence but is made more complicated by the presence of quaternary resonances. The performance of the SEMUT sequence falls off rapidly as the number of bonded protons increases and is particularly poor on the VSP probe. This probably reflects the quality of the 180^{o} proton pulse in this case.

From these unexpected results we suggest that workers carry out similar tests to see which sequence is the most efficient for the particular probes they are using.

Yours sincerely,

Dr. I.H. Sadler.



Probe / Sequence	5 mm Carbon-13 CH	CH_2	CH_3	10 mm V.S.P. CH	CH_2	CH_3	Theoretical CH	CH_2	CH_3
DEPT ($\theta = 3\pi/4$)	0.7	0.8	1.1	0.8	0.7	0.8	0.94	1.33	1.41
APT	1.3	1.0	1.1	1.4	1.0	0.9	1.0	1.0	1.0
SEMUT ($\theta = \pi$)	1.2	0.9	0.6	0.6	0.2	0.0	1.0	1.0	1.0

References

1. D. M. Doddrell, D. T. Pegg, & M. R. Bendall, J. Magn. Reson. 1982, 48, 323.
2. S. L. Patt & J. N. Shoolery, J. Magn. Reson. 1982, 46, 535.
3. H. Bildsøe, S. Donstrup, H. J. Jakobsen & O. W. Sørensen, J. Magn. Reson, 1983, 53, 154

University of Durham Department of Chemistry

Telex: 537351 DURLIB G

Science Laboratories, South Road, DURHAM,
GREAT BRITAIN, DH1 3LE
Telephone: Durham (0385) 64971

Professor of Chemistry:
Robin K. Harris

3rd January, 1986.

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

Dear Barry,

TIN-119 SPECTRUM OF SOLID TRIMETHYLTIN FLUORIDE

In order to stave off further threatening letters from you, we would like to illustrate for TAMUNMR readers the ^{119}Sn spectrum of Me_3SnF in the solid state (Figure 1). This may look complex, but actually most of the lines are spinning sidebands. In fact, there are only three centrebands, indicated by arrows. These are equally-spaced (splitting 1300 Hz) and, integration over the appropriate spinning sideband manifolds shows the true relative intensity is 1:2:1 - a classical first-order pattern, indicating equal coupling <u>two</u> fluorine nuclei. How's that for Me_3SnF? The answer to the conundrum is that there is penta-coordination of tin in the solid state, probably with a chain structure containing Sn···F···Sn···F···Sn bridges. This is also indicated by the low chemical shift in the solid state (δ = +24 ppm with respect to the signal of Me_4Sn).

Analysis of the spinning sideband manifolds yields a lot of information about interplay between the dipolar, indirect coupling (J), and shielding tensors. A crude calculation, using a lot of approximations, yields the data shown in Fig. 2. Don't take the numbers as correct, but simply as indicative of the <u>type</u> of information that can be acquired. I recall Bob Griffin insisting, over dinner in a London restaurant in 1980 that spinning sidebands are a blessing, not a bane. I was sceptical at the time, but I now believe him - except for the type of solid-state ^{13}C work we were carrying out in 1980!

I trust this letter satisfies you for the next nine months or so. Incidentally, the spectrum of Me_3SnF was obtained by Pat Reams on a Bruker CXP 200. Pat has now finished his Ph.D. experimental work and is busy working in industry.

Best wishes for 1986,

Robin

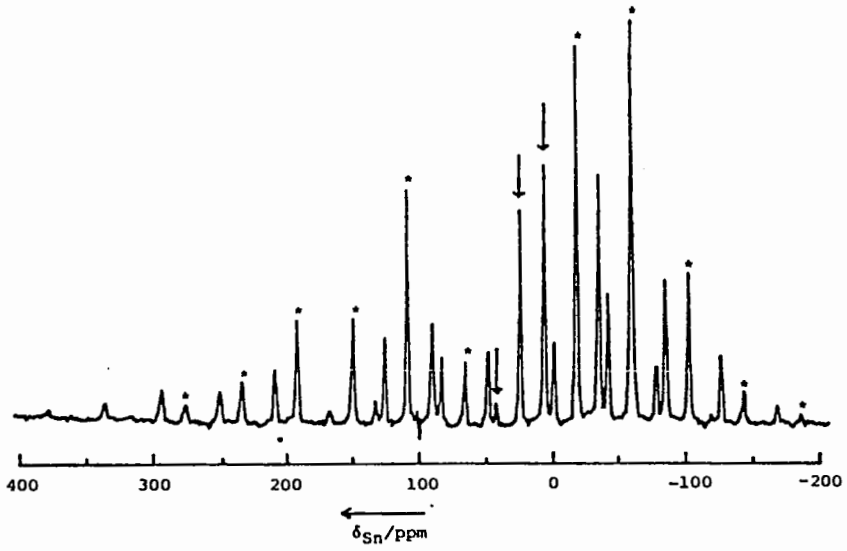
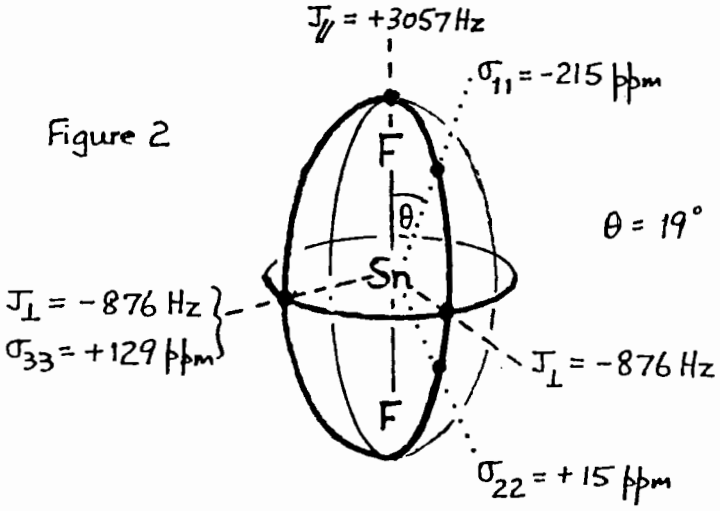


Figure 1. 74.63 MHz ^{119}Sn CP/MAR/HPD NMR spectrum of trimethyl tin fluoride. The three centrebands are indicated by arrows, and the spinning sideband manifold of the middle transition is shown by asterisks. Experimental conditions: number of transients 6000; contact time 2 ms; recycle delay 10 s.

Figure 2



State University of New York
Upstate Medical Center
750 East Adams Street
Syracuse, New York 13210

Department of Radiology
Section of Physics
(315) 473-6510

January 8, 1985

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

Double Quantum Imaging

Dear Barry:

There is much activity in the medical community nowdays involving the use of NMR for diagnosis and as a research tool. For sensitivity reasons proton imaging has received the most attention -- it provides a non-invasive technique to examine ones innards and gives good differentiation of internal structures based on the T_1 and T_2 differences of water (and fat) in the various tissues. The simple spin echo or inversion recovery experiment is the basis for these imaging sequences and involves ordinary transverse and longitudinal magnetization. It is possible to selectively examine materials other than water if one can generate multiple quantum behavior among the protons in more complicated spin systems. This note gives an example illustrating this idea.

The image shown in panel A reflects proton density in the x,z plane of a phantom consisting of three bottles: one filled with Dewar scotch, one with club soda, and one with cheap, French, white burgandy wine. Panel B, on the other hand, was obtained on the identical phantom by generating multiple quantum coherence in those materials that could participate in this behavior, i.e. ethyl alcohol, and then transferring this signal into ordinary transverse magnetization to form the image. The image maps the spatial distribution of alcohol in this case.

A non-selective 90-τ-180-τ-90 sequence was used to generate double quantum coherence, it was subjected to spin warp phase encoding (in the presence of the read gradient), transferred into transverse magnetization with another 90 pulse, and then detected in the presence of the read gradient. The window for the detection period was adjusted so as to only contain the signal corresponding to the double quantum coherence transfer echo. Further phase cycling can be applied to subsequent scans to further reduce any contributions from unwanted signal.

"One drink goes straight to my head ", she said. Experiments dealing with this phenomenon are being investigated.

Best regards,

Nikolaus

Nikolaus M. Szeverenyi

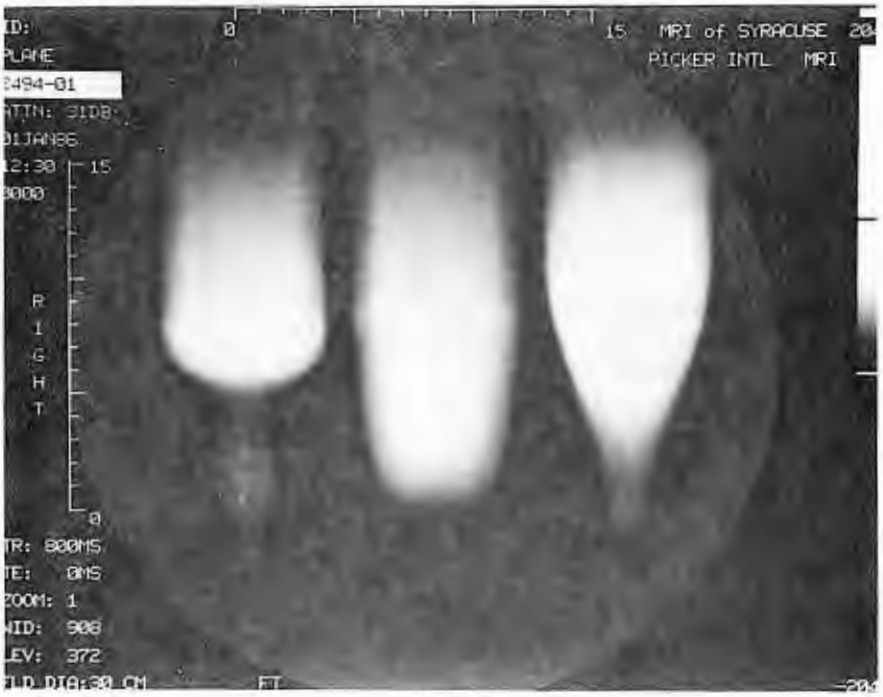


FIGURE A. The proton density image of three bottles (on their sides).

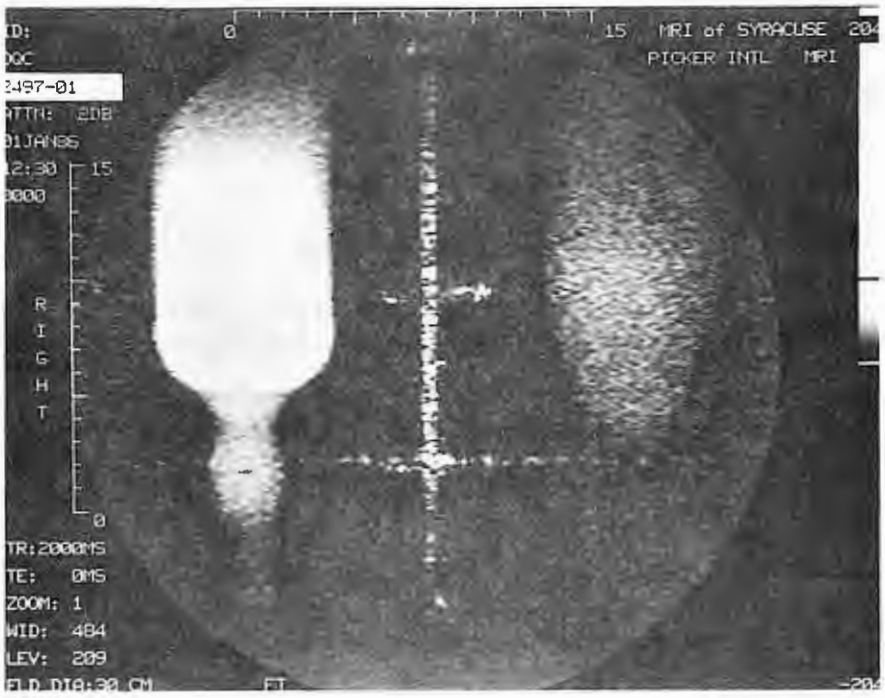


FIGURE B. The same sample as above but imaged using a double quantum excitation and detection scheme. Only those materials in which double quantum magnetization can be generated show up.

These images were obtained on a 0.5 T. Picker clinical imaging unit made available through the courtesy of MRI of Syracuse.

Fachbereich 6
Biologie - Chemie - Geographie

Physikalische Chemie

Prof. Dr. R. Kosfeld

Universität · Gesamthochschule Duisburg

D-4100 Duisburg, 12.11.85
Bismarckstr. 90

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

TX 77843 USA

Structural Analysis of Oligomers

Dear Barry,

in the last year we finished a study on the constitutional and configurational structure of special linear oligomers from vinylchlorid. As reported for oligomers from styrene (see TAMU NMR Letter 316) we identified and completed the structure of the following oligomers separated by HPLC:

DP = 1 1-chloro-3,3-dimethylbutane

DP = 2 1,3-dichloro-5,5-dimethylhexane

DP = 3 threo-1,3,5-trichloro-7,7-dimethyloctane
erythro-1,3,5-trichloro-7,7-dimethyloctane

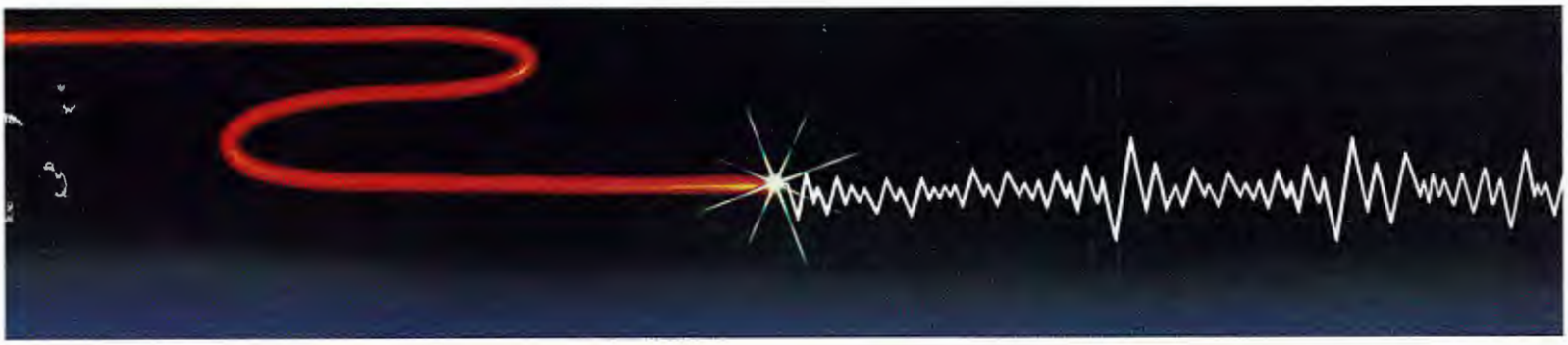
DP = 4 xylo-1,3,5,7-tetrachloro-9,9-dimethyldecane
ribo-1,3,5,7-tetrachloro-9,9-dimethyldecane
arabino-1,3,5,7-tetrachloro-9,9-dimethyldecane
lyxo-1,3,5,7-tetrachloro-9,9-dimethyldecane

Limiting factor is the resolution of HPLC. Though GC has been proven to be the most efficient fractionation procedure it is not recommended for chlorine containing oligomers due to thermal degradation.

With best regards
Yours sincerely

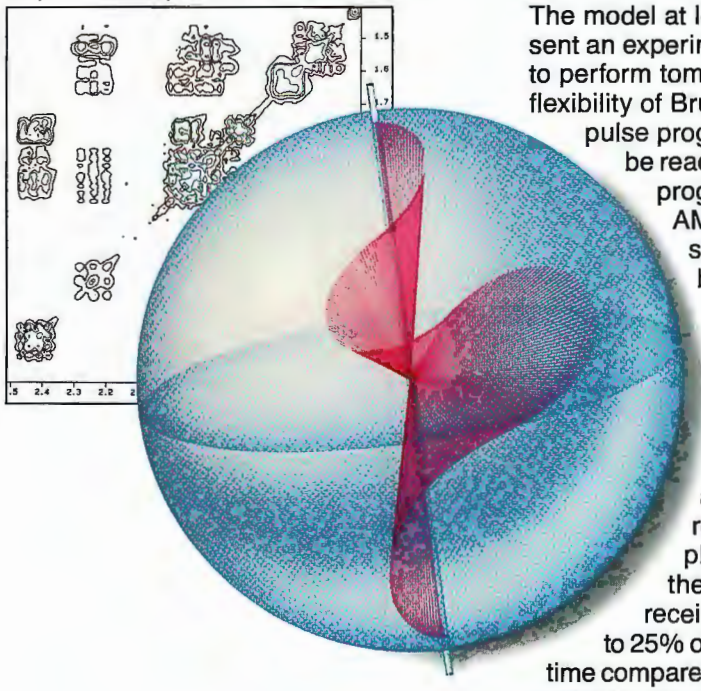
(Prof. Dr. R. Kosfeld) (Dr. K.-F. Elgert)

The NMR evolution continues:



Finally—a pulse programmer that doesn't limit your imagination. Available only with Bruker AM systems.

COSY3 spectrum, 512W x 512W. The experiment time, incl. transform, was less than 15 minutes!



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DOW CORNING

January 17, 1986

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

Subject: $Fe(acac)_3$ as a Simple Qualitative Test for Silanol Presence by ^{29}Si NMR

Dear Professor Shapiro:

In an earlier contribution to this newsletter[1], it was described how the use of paramagnetic $Cr(acac)_3$ could be used for reliable quantitation of silanol species by ^{29}Si NMR. As part of that study, the use of the analogous iron compound, $Fe(acac)_3$, was also evaluated. From consulting the available literature, it was expected that $Fe(acac)_3$ would be a superior relaxation agent to $Cr(acac)_3$ because of its greater magnetic moment, its greater solubility in organic solvent media, and high stability[2].

However, $Fe(acac)_3$ was found to be unacceptable as a general relaxation agent for ^{29}Si NMR spectroscopy. It has been observed that $Fe(acac)_3$ concentrations as low as 5×10^{-4} M will induce extensive and unwanted line broadening in ^{29}Si NMR resonance signals arising from OH-bearing silicons. At a given concentration of $Fe(acac)_3$, the line widths are typically 10-50 times broader than when an equivalent concentration of $Cr(acac)_3$ is used. This phenomenon has been studied in a variety of silanol-functional siloxane and discrete silane species of various chemical forms. The line broadening was verified for all of these species and it appears that this is a universal phenomenon.

It has been found that advantage can be taken of this selective line broadening as a tool to establish whether or not a suspect spectral line is due to the occurrence of silanol functionality. This can be done in a rapid manner and, thus, one can avoid the need to indulge in reactive-type chemistry, such as silazane endcapping(3) to establish silanol presence. Indeed, this method can be effectively employed in situations where chemical derivatization is difficult or inconvenient to do. This point is illustrated below.

In methanol solution, methoxy functional silanes will react with incidental water to form discrete silanol species that are stabilized by the solvent medium[4] and which can be studied by ^{29}Si NMR. Figure 1 is the ^{29}Si NMR spectrum of a ternary model system that was, respectively, 50%, 40%, and 10% by volume of $Et\text{-}Si(OMe)_3$, MeOH and H_2O. This solution, in turn, was prepared in $CDCl_3$ solution with 0.02 M $Cr(acac)_3$ as a relaxation agent. Note the presence of a number of discrete lines in both the silane and siloxane dimer regions of the spectrum. In contrast, the presence of 0.02 M $Fe(acac)_3$ (shown in Figure 2) readily identifies the spectral lines belonging to fully methoxylated species.

FIGURE 1

$EtSi(OMe)_3$ - MeOH - H_2O
(50/40/10 v/v mixture)

^{29}Si NMR Spectrum
0.02 M $Cr(acac)_3$ in $CDCl_3$

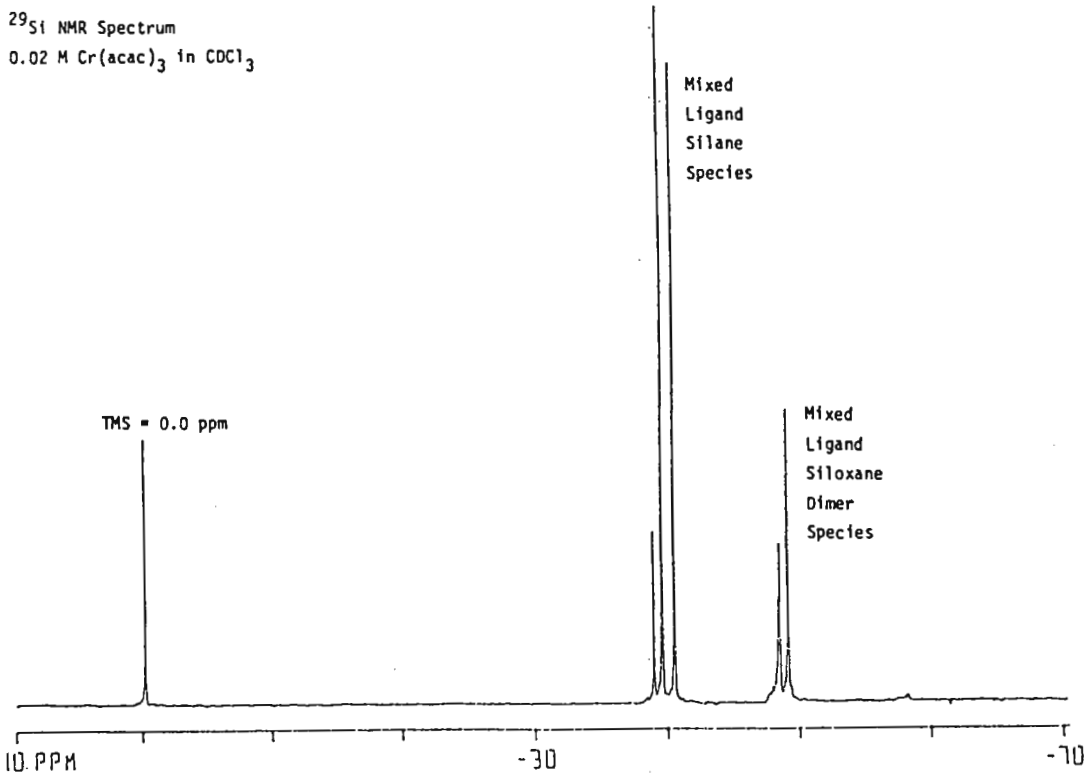
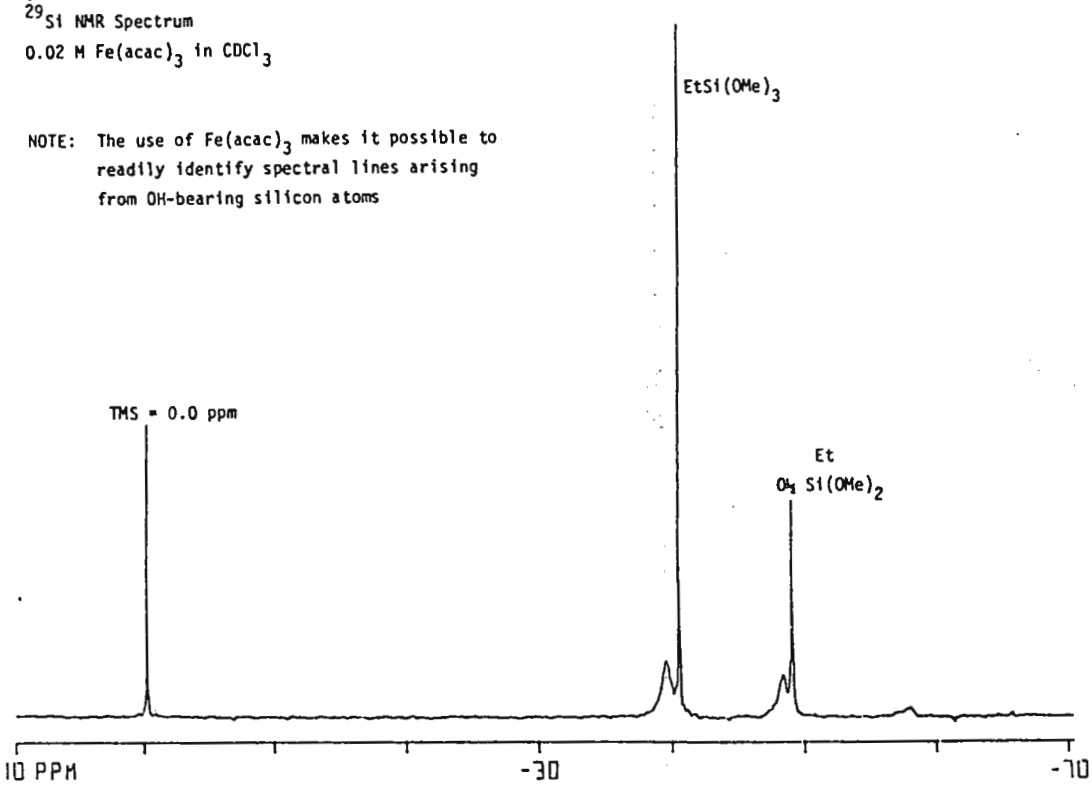


FIGURE 2

$EtSi(OMe)_3$ - MeOH - H_2O
(50/40/10 v/v mixture)
^{29}Si NMR Spectrum
0.02 M $Fe(acac)_3$ in $CDCl_3$

NOTE: The use of $Fe(acac)_3$ makes it possible to readily identify spectral lines arising from OH-bearing silicon atoms



In conclusion, it has been found that this $Fe(acac)_3$-addition technique has been very helpful in our studies of silanol chemistry by NMR.

Sincerely yours,

Thomas M. Carr

Thomas M. Carr
Analytical Specialist
Analytical Research Department

References

1) T. M. Carr and P. J. Garner, Tamu Newsletter, 320, May (1985)

2) G. C. Levy and J. D. Cargioli, J. Mag. Res., 10, 231 (1973)

3) J. H. Gaul and T. M. Carr, Spec. Lett. 16, 651 (1983)

4) C. A. Burkhard, J. Am. Chem. Soc., 67, 2173 (1945)

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Amoco Research Center
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312-420-5111

January 15, 1986

Dr. B. L. Shapiro
TAMU NMR Newsletter
College Station, TX 77843

Quantitative DEPT NMR of Complex Mixtures

Dear Barry:

Recently we used the DEPT NMR experiment to analyze complex mixtures of hydrocarbons such as those one encounters in petroleum products. We wanted to test the quantitative nature of this experiment. Toward this end, we have prepared a few known mixtures of pure compounds which might be expected to be found in a petroleum product. The composition of two synthetic blends is contained in Table I. This table shows the weight percent and mole percent composition of blends A and B. Table II shows the NMR data for the various carbon types in the blend based on the number of attached protons in the aromatic and aliphatic regions of the spectrum and compares these values with those calculated from the composition of the mixtures. Definition of the various terms used in Table II are listed in the table. Examination of the data in Table II indicates that with proper care in setting the DEPT parameters, the experiment can be made reasonably quantitative. We have only begun our investigation of this technique but these preliminary results look quite promising as regards the use of this powerful spectral editing procedure in the analysis of complex mixtures. Please credit this contribution to the account of C. J. Ray.

Sincerely,

Bill Dunlap

R. W. Dunlap, F-9
(312) 420-5154

Charles Price

C. T. Price, F-9
(312) 420-5782

JH26:RWD/9907
Attachment

Table I

Composition of Blends

Component	Blend A		Blend B	
	Wt%	Mole%	Wt%	Mole%
phenanthrene	4.4	3.3	2.8	2.5
methyl naphthalene	15.6	16.1	9.9	10.8
dimethyl naphthalene	1.2	1.1	1.1	1.1
trimehyl benzene	6.4	7.8	5.5	6.9
tetramethyl benzene	7.2	7.8	5.2	6.0
t-butyl benzene	7.1	7.7	5.6	6.5
phenyl dodecane	6.5	3.9	5.5	3.5
cyclohexyl benzene	5.9	5.4	6.1	5.9
n-undecane	5.6	5.3	4.9	4.9
n-nonane	5.7	6.5	5.1	6.2
trimethyl pentane	5.1	6.5	7.2	9.8
dimethyl octane	6.2	6.3	5.6	6.1
dimethyl cyclohexane	6.3	8.2	6.1	8.4
methyl undecane	6.2	5.3	6.9	6.3
decalin	5.6	5.9	4.7	5.3
eicosane	4.9	2.5	17.7	9.7

Table II

DEPT NMR Results

Parameter	Blend A		Blend B	
	Calc	Meas	Calc	Meas
%CA	39.0	39.2	29.0	29.6
%CA-H	26.0	26.3	19.5	19.8
%CA-C	13.0	12.1	9.5	8.4
%C-CH	5.4	5.6	5.5	8.4
%C-CH2	33.8	34.6	43.6	43.6
%C-CH3	20.4	20.1	20.5	18.1
%C-q	1.3	1.2	1.4	1.7

%CA= % aromatic carbons total
%CA-CH= % aromatic carbons bearing a hydrogen
%CA-C= % aromatic carbons bonded to other carbons
%C-CH= % aliphatic methine carbons
%C-CH2= % aliphatic methylene carbons
%C-CH3= % aliphatic methyl carbons
%C-q= % aliphatic quaternary carbons

RWD/jh

International Business Machines Corporation

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January 23, 1986

Prof. B. L. Shapiro
Dept of Chemistry
Texas A & M University
College Station, TX 77843-3255

Dr. Shapiro, "X Nucleus Decoupling with Scraps"

This is the first report from our new laboratory, which is called the Almaden Research Center, which is high on a hill overlooking Silicon Valley and other very expensive real estate. I think it is also the first report from IBM Research San Jose by anybody except Nino Yannoni. I will spare the gory details of what it has been like to move several large spectrometers since it is another example of the event we all have to deal with called "dealing with reality"!

Several articles in the TAMU newsletter have dealt with decoupling of one kind or another, including some about using an "x" nucleus decoupler accessory on newer Bruker spectrometers. I would like to pass on a method of using a frequency mixer to generate the x nucleus frequency "on the cheap". Basically, one taps off the decoupler frequency and mixes this with a referenced synthesizer frequency to get the desired decoupling frequency. On a Bruker designed spectrometer, the schematic below permits one to also use the O2 settings as well as most of the decoupler amplifier circuitry. The BB Modulation board will work, too! By using the attenuated signal from the decoupler as the input to the observe preamplifier, you can match the decoupler and the x nucleus observe frequencies by adjusting the synthesizer frequency until there is no sine wave in the FID and the spike in the transform is where the observe pulse would ordinarily be. Thus, you can carry out selective decoupling and know that the offsets are correct. You will probably have to use a power amplifier to get the output power up. I have been able to carry out fluorine decoupling of carbon NMR with relative ease.

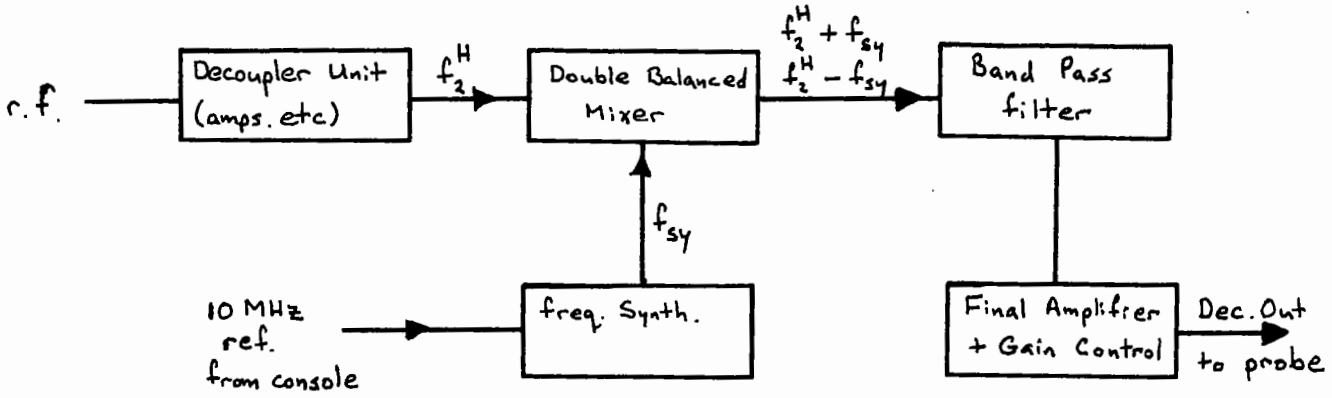
I should also mention that I looked at the broad band irradiation of the decoupler of an NR/80 Bruker designed spectrometer. I found that if the potentiometer P1 on the modulator board is adjusted, one can get a band width of as much as 6 kHz. This has been useful for carrying out fluorine decoupled carbon experiments where the chemical shift range necessary is much larger than that for protons. Since this board is fairly standard on Bruker spectrometers, this may be useful for others who need to decouple fluorine but do not have access to WALTZIAN pulse sequences. A copy of the measurement is included.

The machines will be running soon so that I should be able to include some spectra next contribution. Best wishes to all!

Sincerely,

Bill Fleming

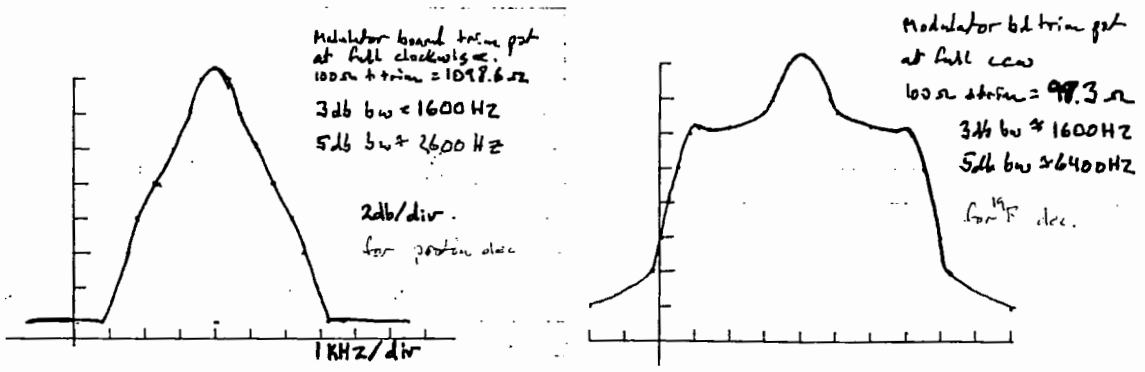
W. W. Fleming



f_2^H = proton dec. freq.; f_2^X = either $(f_2^H + f_{sy})$ or $(f_2^H - f_{sy})$

X Nucleus Decoupling Modification

Using Scraps, Homemade, and Cheap Parts



Data From Modulator Board Adjustments

Professeur PIERRE LASZLO

Institut de Chimie
Université de Liège
Sart-Tilman par 4000 Liège 1, Belgique

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

January 13,1986

Pr^{3+} TRANSPORT ACROSS PHOSPHOLIPID VESICLES IN THE JOINT PRESENCE OF AN IONOPHORE AND A FATTY ACID

Dear Barry,

We have earlier reported a remarkable synergism in the transport of Pr^{3+} across phosphatidylcholine vesicles when two carboxylic ionophores are incorporated into the lipid bilayer (1,2).This effect has been attributed to the presence of a ΔpKa in the 2:1 hybrid complex, which increases the H^+ (Na^+) countertransport. Using P-31 NMR,we have tested this hypothesis by studying Pr^{3+} transport (to distinguish inner from outer compartments) in the joint presence of an ionophore and a fatty acid.Indeed,cation transport mediated by X-537A is accelerated in the presence of a fatty acid,provided a long-enough alkyl chain (C_{10}) gives it enough lipophilicity for incorporation into the lipid bilayer.
The following factors were considered:
-increase of negative charge density at the interface;
-perturbation of the bilayer structure;
-chemical change in the composition of the membrane lipids;
and all ruled out by appropriate experiments.
Kinetic results on Pr^{3+} inflow and on proton efflux showed that they are coupled, which explains the observations.

Jean Grandjean

Pierre Laszlo

(1) J.Grandjean,P.Laszlo,(1984),J.Am.Chem.Soc.,106,1472-6
(2) R.A.Bartsch,J.Grandjean,P.Laszlo,(1983),Biochem.Biophys.Res. Commun., 117,340-3.

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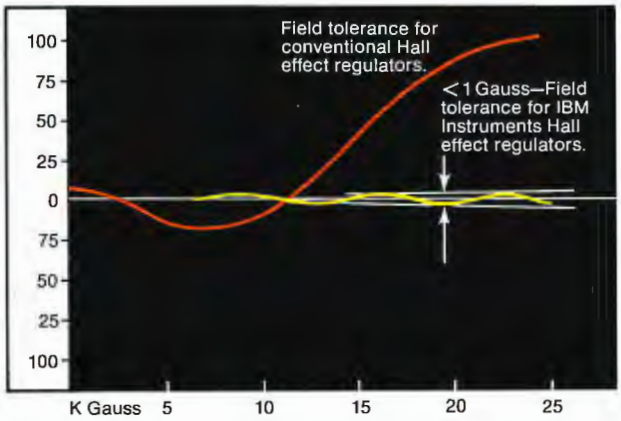

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January 23, 1986

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

Dear Barry:

Partial deuteration of the SH groups of molecules such as 2-mercaptoethanol and cysteine derivatives gives rise (under conditions of slow hydrogen exchange) to isotopic multiplets in their carbon-13 NMR spectra. An example is shown in the Figure. These are the isotopic multiplets in the spectrum of a mixture made up of 2-mercaptoethanol and methanol-d_1 in C_6D_6 as the solvent. The carbon atom bearing the thiol group appears as a doublet of doublets due to a two-bond isotope effect from the SH/SD group and a three-bond isotope effect from the OH/OD group. The carbon atom attached to the hydroxyl group exhibits only a two-bond effect. The much larger protium/deuterium ratio for the thiol group relative to that of the hydroxyl group is rather conspicuous. Deuterium/protium fractionation factors were determined directly from the integrated intensities of the multiplet components. The fractionation factor for the SH group (relative to water) was found to be in the range 0.44 $\pm$ 0.01 and independent of the substance.

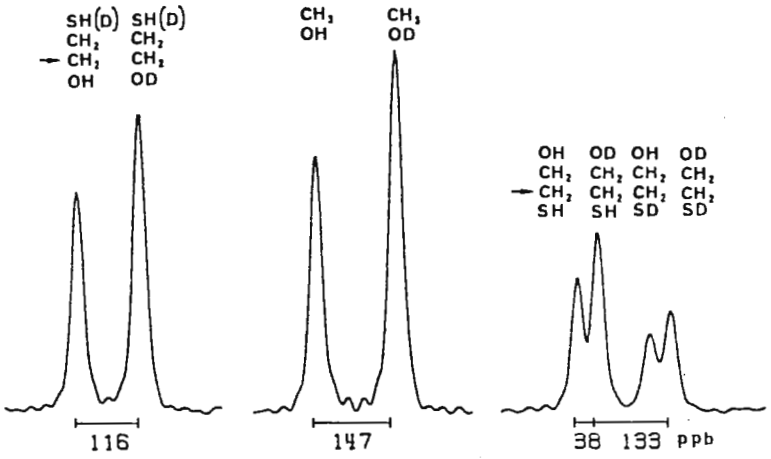
Please credit this contribution to the Hercules Research Center subscription.

Title: Isotopic Multiplets in the Carbon-13 NMR Spectra of Thiols with Partially Deuterated Hydroxyls.

Sincerely yours,

Jacques

Jacques Reuben



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IN REPLY REFER TO:
6120-64:JBM:erj
January 27, 1986

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

Refocussed Gradient Imaging:
Removal of Static Field Inhomogeneity and Chemical Shift Effects

Dear Barry,

For some time we have been interested in NMR imaging of solids. Our efforts have centered on combining imaging techniques with line-narrowing techniques, in order to enhance spatial resolution. During the course of our work with solids, we have developed a method for eliminating distortions in liquid-state images due to static field inhomogeneity, chemical shift, and bulk susceptibility. We refer to the technique described below as refocussed gradient imaging.

The pulse sequence and gradient timing for one-dimensional refocussed gradient imaging are shown at the top of the figure. The r.f. consists of a CPMG pulse train with π-pulse spacing of 2τ. The gradient is amplitude-modulated sinusoidally with a period of 4τ. The CPMG sequence refocusses at $2n\tau$ the spin evolution due to static field inhomogeneity, chemical shift, and bulk susceptibility; however synchronous refocussing of the spins and the gradient allows the gradient evolution to continue unabated. Thus Fourier transformation of the time evolution of the magnetization stroboscopically detected every $2n\tau$ produces an image with no distortions from the above-mentioned effects.

We demonstrate the technique on a sample of three capillary tubes (1.2mm i.d.) containing $CoCl_2$ doped water which are aligned parallel to dB/dz. The 1-D proton (58MHz) image labelled "a" was obtained with a static gradient method while "b" was obtained with the refocussed gradient method. The images are qualitatively the same. When a 7mm length of steel paper clip is

inserted into the probe to within 9mm of the capillary labelled #1, images "c" (static gradient) and "d" (refocussed gradient) are obtained. Image "c" is unrecognizable; we estimate the image of tube "1" to be shifted by about 6kHz and broadened on the order of 4-5kHz. In contrast, only a small distortion of the refocussed gradient image is observed. This distortion may be due to time-dependent magnetic fields induced in the steel paper clip.

This work will be reported in J. Magnetic Resonance.

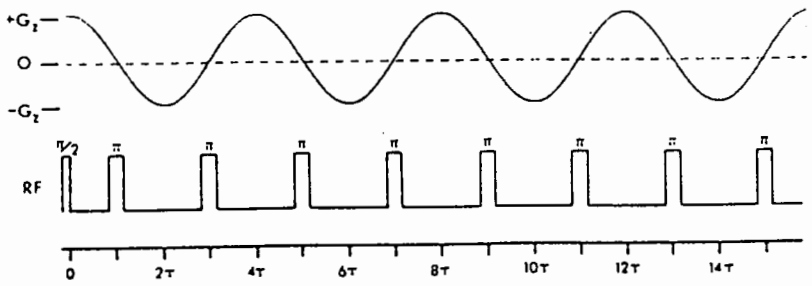
Sincerely yours,

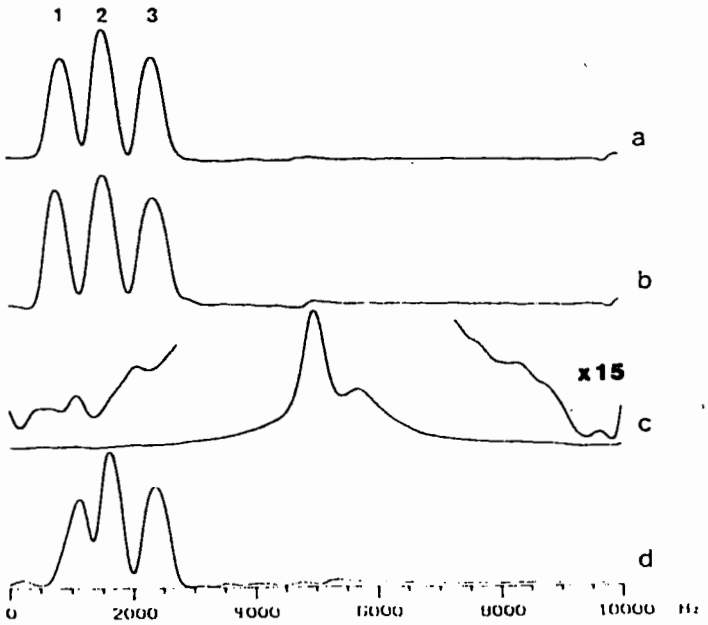
Joel

AI

Joel B. Miller
NRC/NRL Postdoctoral Associate
Polymeric Materials Branch
Chemistry Division
Code 6120

Allen N. Garroway, Head
Polymeric Diagnostic Section
Polymeric Materials Branch
Chemistry Division
Code 6120





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221 Longwood Avenue
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January 28, 1986

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

Re: Na-23 NMR and Ischemia

Dear Professor Shapiro,

We are utilizing Na-23 NMR in combination with shift reagents (SR) for cations to observe changes in intracellular sodium during control perfusion, ischemia and reperfusion in the rat heart. Measurements were made on isolated, perfused, isovolumically-contracting rat hearts at 95.24 MHz with 90 degree pulses and a pulse recycle time of 250 msec. The hearts were perfused with a Krebs-Henseleit buffer with 10 mM Na DyTTHA (1). The basic protocl for these experiments consisted of a 28 min control period, a 28 min ischemic period initiated by stopping the flow of the mannitol bath and the perfusate to the heart, and a 28 min post-ischemic period of flow to the bath and heart. Na-23 NMR spectra were acquired continuously throughout the entire protocol with one min time resolution.

The results are shown in Figure 1. Figure 1a is a stacked plot of the Na-23 NMR spectra obtained during control perfusion of a rat heart in the presence of SR in the perfusate and the bath. We make the following assingnments: The downfield portion from 6 to 9 ppm is due to sodium in the mannitol bath; the large peaks from 2 to 6 ppm are due to sodium in the vascular and interstitial spaces of the heart and possibly the bath; and a small highfield shoulder on the large peaks at about 1 ppm corresponds to the intracellular sodium. The total area of the spectrum increases about 10% during the course of the control period; this increase is limited to the downfield signals representing sodium in all the extracellualar spaces. The area of the intracellular sodium is relatively constant. During ischemia (Figure 1b) large changes are observed in the spectrum. Much of the shifted area representing extracellular sodium moves about 2 ppm further downfield. This is due to a loss of sodium from the vascular spaces of the heart. The area of the unshifted peak reperesenting the intracellular sodium resonance increases 3 to 4 fold during ischemia. Upon resumption of flow to the bath and heart (Figuer 1c) the position of the extracellular resonances is now found at the same chemical shift as observed during control period. The area of the intracellular sodium peak decreases but not to control levels. The extracellular resonance areas increases throughout the period of reperfusion.

(continued on page 37)

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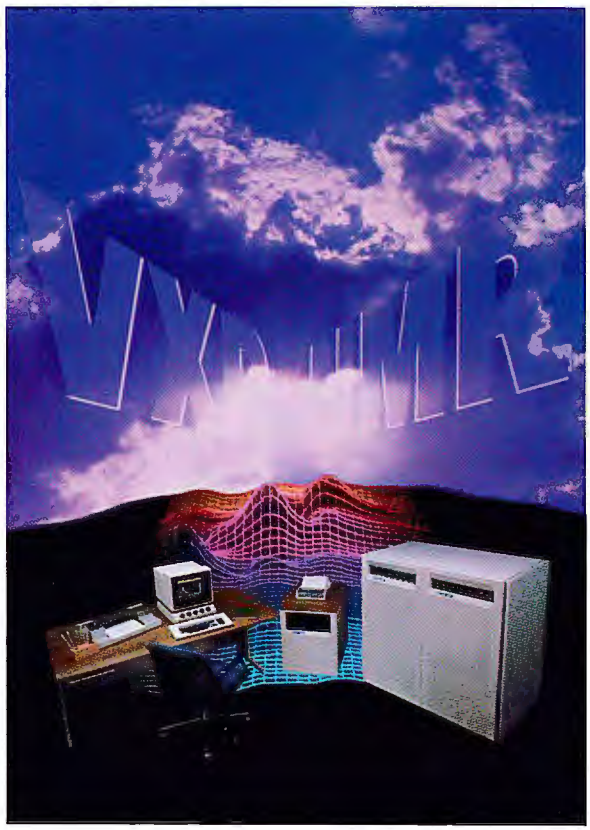

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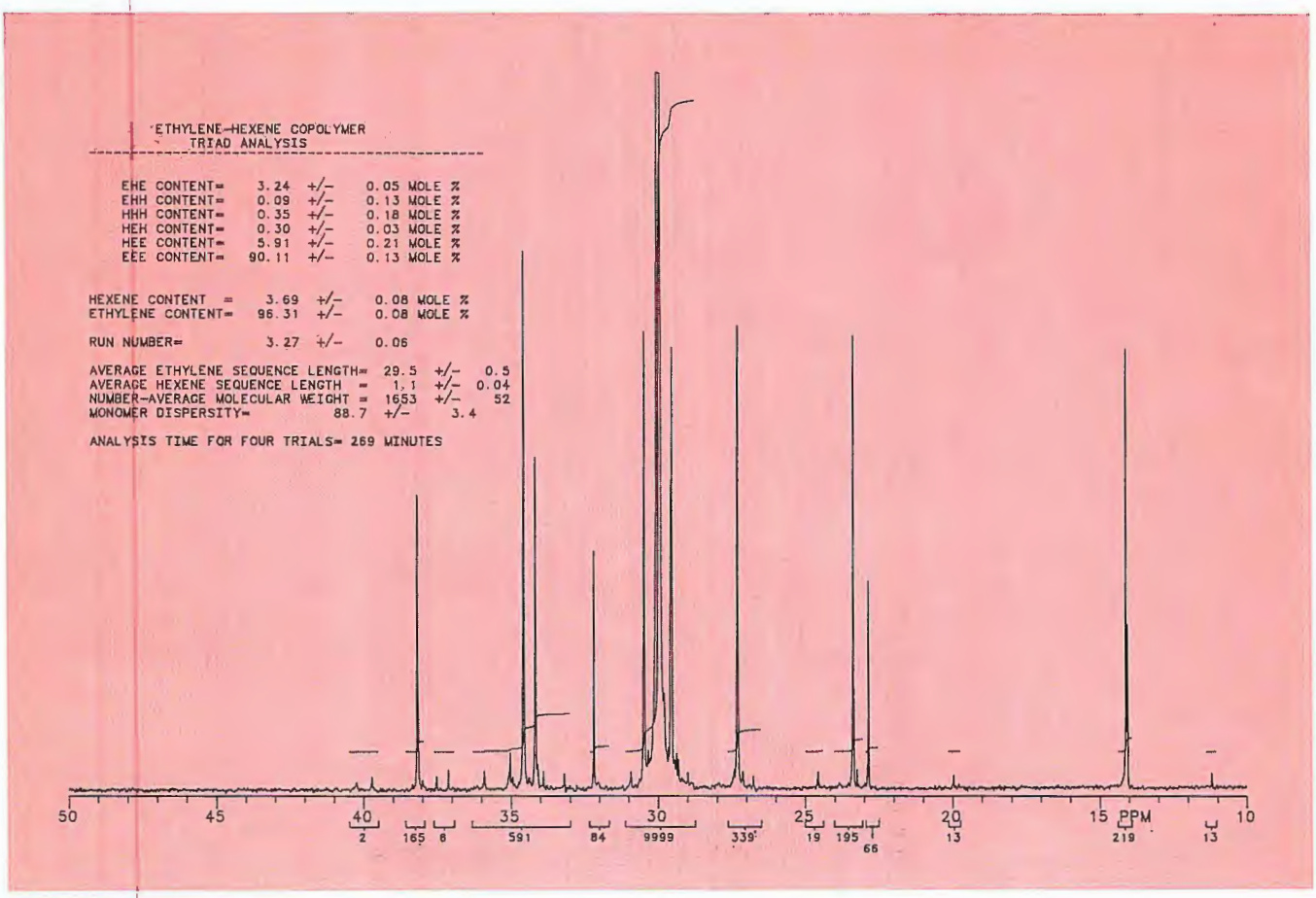

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(continued from page 34)

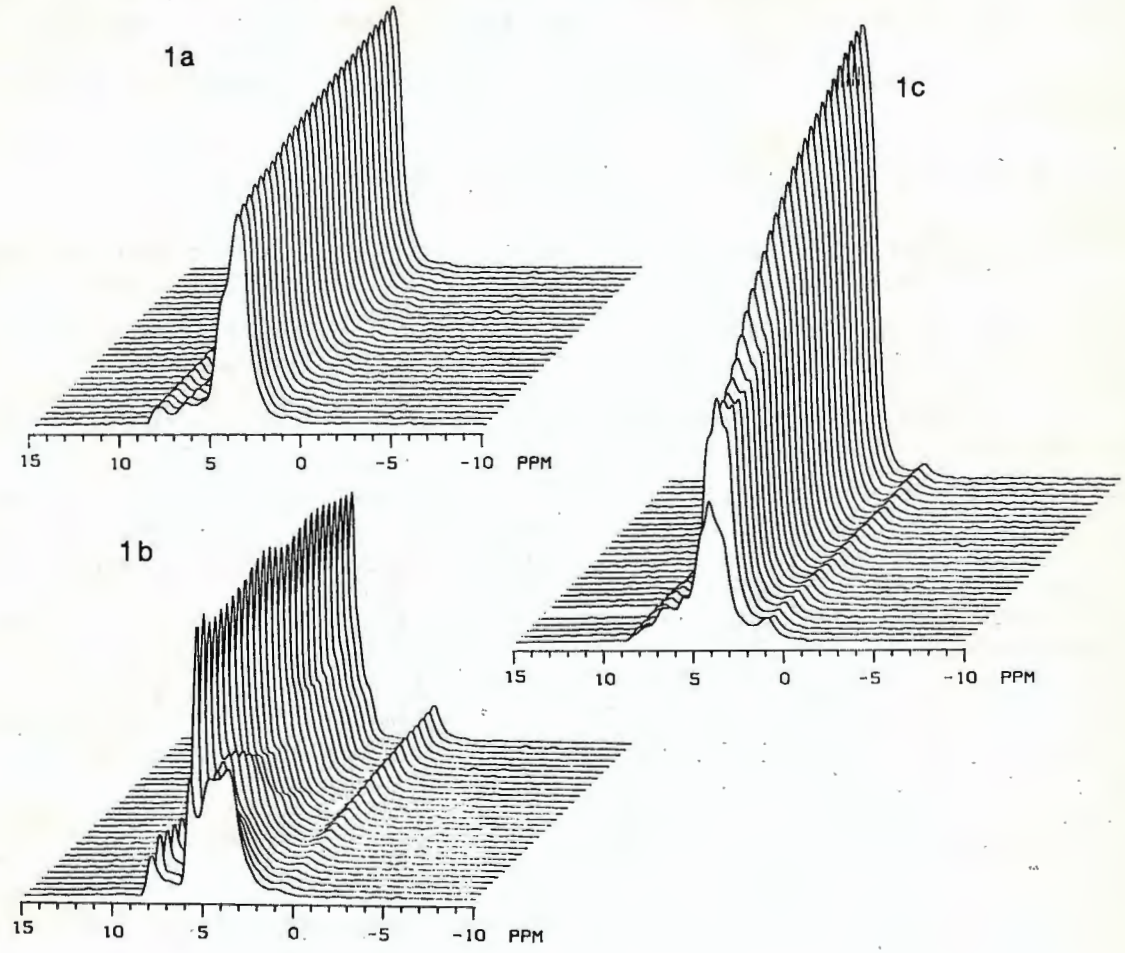
Thus, utilizing SR and Na-23 NMR, we have observed an accumulation of intracellular sodium in the ischemic rat heart. The continuous increase in the extracellular peaks during the post-ischemic period is caused by edema, and is consistent with injury caused by the ischemia. We believe these results show that the combination of SR and Na-23 NMR will be valuable tools to define the events that occur during ischemia in the heart.

Sincerely,

James A. Balschi

Joanne S. Ingwall

(1) M.M. Pike, J.C. Frazer, D.F. Dedrick, J.S. Ingwall, P.D. Allen, C.S. Springer, Jr. and T.W. Smith (1985) Biophys. J. 48, 159.



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

January 30, 1986

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

Relaxation in Detergent Micelles, Monomers and Bulk Hydrocarbons

Dear Professor Shapiro:

We have extended our interest in ^1H NOE studies of phospholipid membranes to studies of detergent micelles and related solutions in an attempt to understand more fully the ^1H spin relaxation of 361 MHz in these types of systems. Recently Söderman, Stilbs and coworkers have studied spin lattice relaxation in spherical micelles over a wide range of resonance frequencies and found that the relaxation could be explained in terms of two types of motion: a) fast motions due to bond rotations, torsions, etc. and b) slower motions due to micelle rotation and intramicellar diffusion.[1,2] Both a) and b) could be characterized by single correlation times. The appropriate spectral density function is:

$$J(\omega) = (1-S^2)\ 2\tau_c^f/1+(\omega\tau_c^f)^2 + S^2 2\tau_c^s/1+(\omega\tau_c^s)^2$$

where S is the usual order parameter and the superscript f and s denote fast and slow motions. Previous NMR and other structural information allowed us to calculate $S^2 2\tau_c^s/1+(\omega\tau_c^s)^2$ for SDS micelles and we find that $\geq$ 98% of the ^1H relaxation at 361 MHz is due to the fast motions. This allowed us to obtain the fast motion correlation times shown in Fig. 1 in a fairly direct manner. As one can see, the fast motion rates for dodecane and monomeric SDS are similar and only a factor of 1.5 greater than those for micellar SDS.

We have also measured steady state ^1H NOE's for the above samples (Fig. 2). The presence of negative NOE's indicates that the slow motions make a substantial contribution, unlike the case of spin lattice relaxation. The order parameters in micelles are small (<0.25) so they don't affect the fast spectral density term much but do affect the slow term. The sensitivity of the NOE to the slow term suggests that the NOE may yield information about molecular order in this type of system. Further analysis is in progress. The negative NOE seen at the $(CH_2)_n$ position after saturation of the ωCH_3 is partially due to the "three spin effect".[3] The similarity of the micelle and monomer SDS NOE's and the fact that they are slightly smaller than the analogous dodecane NOEs may indicate that 5 mM SDS is not completely monomeric.

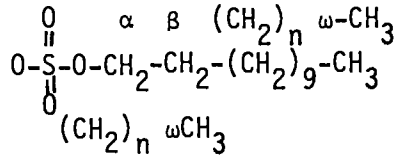
1.) Walderhaug, H.; Söderman, O., and Stilbs, P. (1984) J. Phys. Chem. 88, 1655-1662.
2.) Söderman, O.; Walderhaug, H.; Henriksson, U. and Stilbs, P. (1985) J. Phys. Chem 89, 3693-3701.
3.) Noggle. J.H. and Schirmer, R.E. (1971) The Nuclear Overhauser Effect, Academic Press, New York, p. 59.

Jeff Ellena

Raymond Dominey

David Cafiso

Sodium Dodecyl-Sulfate



Dodecane $CH_3(CH_2)_{10}-CH_3$

Figure 1

τ_c^f(ps)

solution	position α	β	$(CH_2)_n$	ωCH_3
0.3M SDS (micelles)	35	50	47	12
5 mM SDS (monomers)	24	33	30	7
dodecane			25	8

Figure 2

% ^1H NOE

position observed		position saturated α	β	$(CH_2)_n$	ωCH_3
α	a		5.0		
	b		8.7		
	c		—		
β	a	4.7		-8.2	
	b	2.6		-2.1	
	c	—			
$(CH_2)_n$	a		-4.3		-4.2
	b		-4.8		-7.1
	c		—		-1.3
ωCH_3	a			2.8	
	b			2.7	
	c			6.8	

a = 0.3 M SDS; Δ = 5 mM SDS; c = dodecane

(with one exception only NOEs with an absolute value > 1.5% are listed, uncertainty in NOEs observed at the α and β positions is ~ 1.5% and at the $(CH_2)_n$ and CH_3 positions uncertainty is ~ 1.0%.)

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January 24, 1986

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

Dear Professor Shapiro:

I am currently building a broadline NMR spectrometer to enable ^{2}H and ^{31}P NMR studies of membranes. Assembly of the transceiver represents the major construction task, existing equipment within the Physics Department at IUPUI being utilized for the remainder of the spectrometer. The computer system (Nicolet 1080, 293 I/O controller and Diablo disk drive, etc.), however, leaves a lot to be desired. Thus, I should be very grateful to hear from anyone who wishes to dispose of alternative equipment.

Yours sincerely,

Steve Wassall

S. R. Wassall
Assistant Professor

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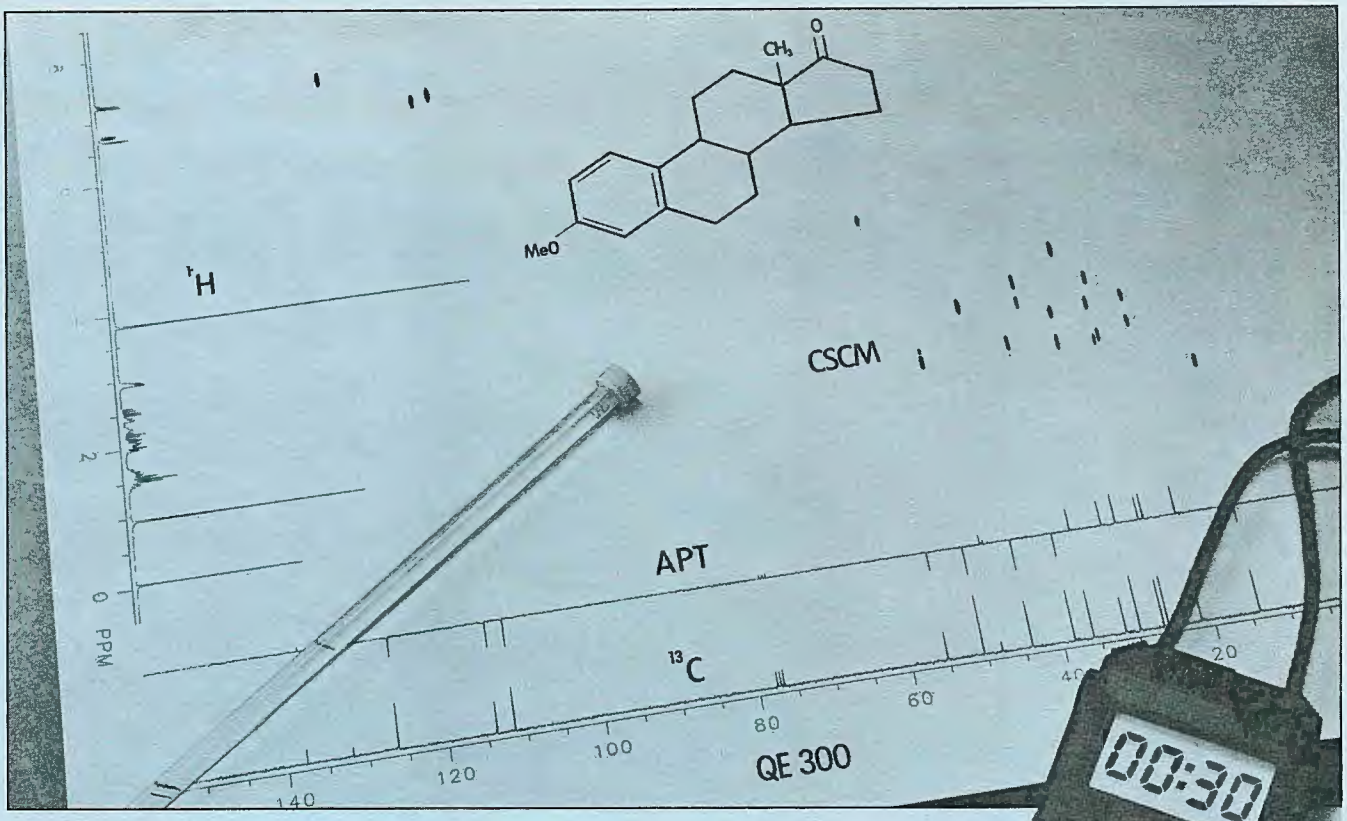
The Center for Biological NMR at Texas A&M University invites application for the position of Research Scientist (NMR specialist) to maintain and operate two Bruker instruments (300 MHz WB, 500 MHz) which are used for experiments with enzymes and biological materials. The successful candidate should have extensive (at least 5 years) experience in hardware and software modifications and be capable of designing and assisting with experiments involving the acquisition of data in vivo (perfusion) and in vitro (enzymes, substrates and inhibitors) at low temperature. A doctorate in physical chemistry, electrical engineering, physics or chemical physics and the ability to work as a team member with organic chemists, biochemists and biologists are required. The position is permanent and in the salary range $30,000-$35,000, depending on experience. The appointment could be made at the Senior Scientist level ($35,000-$50,000) in the case of a very experienced candidate. Application including CV and the names of three referees should reach Mrs. Jean Long (Administrative Assistant), CBNMR, Department of Chemistry, Texas A&M University, College Station, Texas 77843, as soon as possible but no later than April 30.



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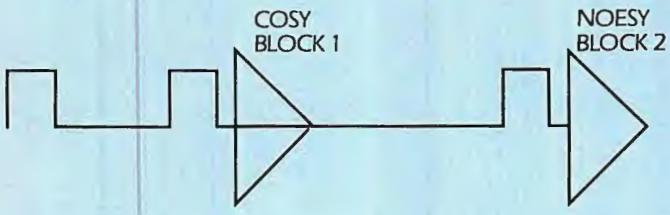

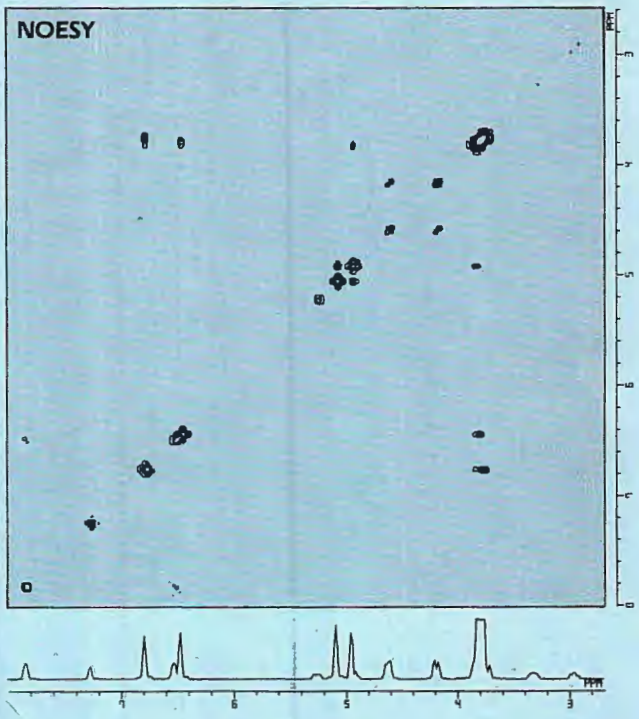

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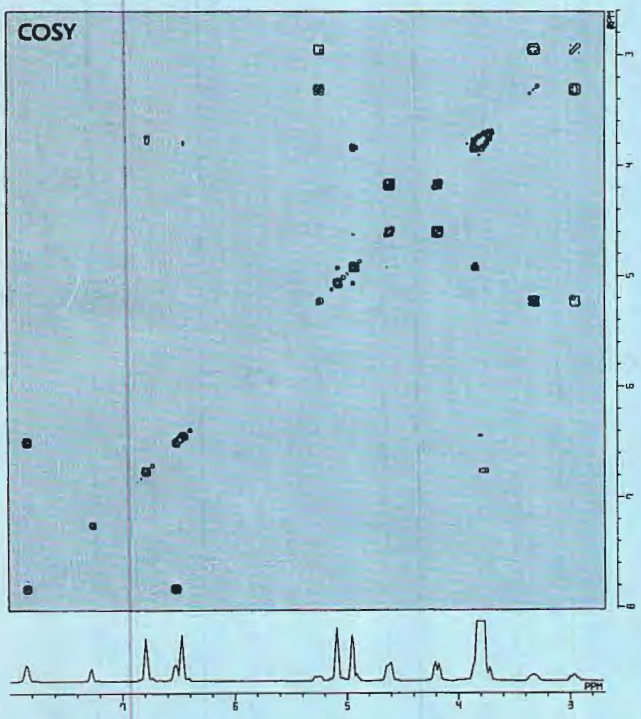

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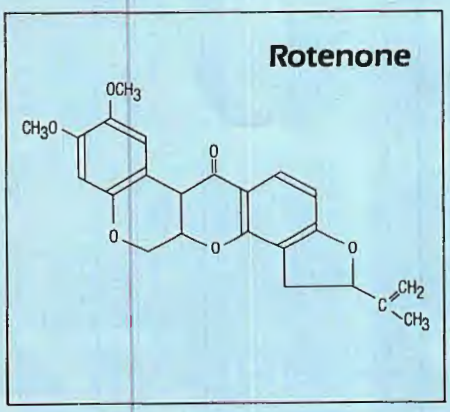

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