TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 355

April 1988

Continued on page 84

Announcing... AN OUTSTANDING ADDITION TO THE

WILMAD NMR LINE...

our COMPLETELY NEW 5mm "THRIFT" TUBE

at 95¢ each!

- ***INEXPENSIVE***
- ***PRACTICAL***
- ***RELIABLE***
- ***GUARANTEED***

...THE BEST POSSIBLE ANSWER FOR LOWER-END NMR SPECTROSCOPY NEEDS.

COMPARE THESE OUTSTANDING FEATURES OF OUR NEW WG-5mm-THRIFT-7 TUBE:

- **100% Wilmad inspection of structural parameters.**
- **Spinning Reliability. Passes our stringent Spinner Bearing Test which determines straightness and spinning stability using a Precision Bore Bearing just 0.002″ larger than the tube O.D. No halted data accumulations or scratched tubes. Send for your free 5mm Spinner Bearing today.**
- **Round bottom is standard. Flat bottom . . . no extra charge.**
- **Non-Pyrex compatible borosilicate glass.**
- **Packaged individually for maximum protection.**
- **Standard length is 7″. Available in 8″ and 9″ lengths. (Add 15¢ per inch.)**
- **Immediate shipment from available stock.**

The Wilmad 5mm THRIFT tube is one of the most important recent developments in NMR tube manufacture. It is not recommended for use in high resolution spectrometers, but it provides exceptional performance in lower-end spectroscopic investigations and, at the same time, retains its low cost. It is manufactured from Non-Pyrex compatible borosilicate drawn tubing and is carefully selected for size and structure. At 95¢ each, this tube is really a bargain.

In fact, it is an infinitely better bargain **in both price and quality** than the following Norell tubes: 508-UP ($4.50 each); 507-HP ($3.50 each); 506-P ($2.50 each); 505-P ($1.80 each); XR-55 ($2.00 each); and 502 (80¢ each). Our examination of numerous Norell tubes has shown that the only significant difference between them is price. They consistently fail to meet even the most liberal structural standards used to define them.

Even with our less expensive 5mm THRIFT tubes, you'll soon learn why IT PAYS TO STANDARDIZE ON WILMAD!

WILMAD GLASS COMPANY, INC.

Serving the Spectroscopic Aftermarket

Route 40 and Oak Road, Buena, NJ 08310, U.S.A.

Phone: (609) 697-3000 • TWX 510-687-8911

TEXAS A&M NMR NEWSLETTER NO. 355, APRIL 1988 AUTHOR INDEX

TEXAS A&M NMR NEWSLETTER NO. 355, APRIL 1988 ADVERTISER INDEX

SPONSORS OF THE TAMU NMR NEWSLETTER

Abbott Laboratories
The British Petroleum Co., Ltd. (England)
Bruker Instruments, Inc.
Cryomagnet Systems, Inc.
The Dow Chemical Company
Eastman Kodak Company
E. I. du Pont de Nemours & Company
General Electric Company, Medical Systems Group, NMR Instruments
Intermagnetics General Corporation
JEOL (U.S.A.) Inc., Analytical Instruments Division
The Lilly Research Laboratories, Eli Lilly & Company
Millipore Corporation, Waters Chromatography Division
The Monsanto Company
New Methods Research, Inc.
Norell, Inc.
The Procter & Gamble Company, Miami Valley Labs
Programmed Test Sources, Inc.
Shell Development Company
Spectroscopy Imaging Systems Corporation
Spectral Data Services, Inc.
Unilever Research
Union Carbide Corporation
Varian, Analytical Instrument Division

FORTHCOMING NMR MEETINGS

9th EENC (European Experimental NMR Conference), May 16-20, 1988; Bad Aussee, Austria; For further information, write Professor H. Sterk, Karl-Franzens-Universitaet Graz, Institut fuer Organische Chemie, Heinrichstrasse 28, A-8010 Graz, Austria. See Newsletter 348, 15.

Teaching Course on Nuclear Magnetic Resonance, May 30 - June 3, 1988; Trondheim, Norway; Ms. I. S. Gribbestad, The MR Center, N-7034, Trondheim, Norway.

European Workshop on Nuclear Magnetic Resonance: Seminar on Relaxometry, June 6-7, 1988; Trondheim, Norway; Ms. I. S. Gribbestad, The MR Center, N-7034, Trondheim, Norway.

2nd European Congress on NMR in Medicine and Biology, June 23-25, 1988; Berlin, West Germany; contact Prof. R. Felix, Dept. of Radiology, Charlottenburg University Hospital, Spandauer Damn 130, D-1000 Berlin 19, West Germany.

XIII Intl. Conference on Magnetic Resonance in Biological Systems, Aug. 14-19, 1988; Madison, Wisconsin. See Newsletter 349, 60.

NATO Summer School: "A Methodological Approach to Multinuclear Magnetic Resonance in Liquids and Solids: Chemical Applications", August 22 - September 2, 1988; Maratea, Italy; See Newsletter 353, 76.

XXIV Ampere Congress on Magnetic Resonance and Related Phenomena, August 29 - September 3, 1988; Poznan, Poland; Dr. S. Hoffmann, Instytut Fizyki Molekularnej PAN, ul. Smoluchowskiego 17/19, 60-179 Poznan, Poland.

Continued on page 21

All Newsletter Correspondence Should Be Addressed To:

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303, U.S.A.

(415) 493-5971

DEADLINE DATES

No. 357 (June) ———— 20 May 1988
No. 358 (July) ———— 17 June 1988
No. 359 (August) ———— 22 July 1988
No. 360 (September) —— 19 August 1988

NMR Studies of Polyamine-DNA Interactions

Michael J. Minch*, Yong Ma and James Blankenship
Departments of Chemistry and Pharmacology
University of the Pacific
Stockton, CA 95211

(received 2/25/88)

Polyamines are aliphatic polycationic compounds found in all cells. A large body of data, collected over the last two decades, indicates that polyamines must play an essential role in cell growth and differentiation. Their ubiquitous distribution, their high concentration in cells, the increase in their concentration in rapidly growing tissue and the coordination of their acetylation and deacetylation with the cell cycle all point to a prominant role for such polycations. Yet their specific physiological function is not known although it is generally presumed that polyamines affect growth by interacting with DNA. There is ample experimental and theoretical evidence for strong binding between polyamine and DNA accompanied by profound DNA conformational changes. Characterization of a polyamine-nucleic acid complex involves more than an estimation of the binding forces, which was the focus of earlier studies, or even the average or lowest energy structure of the complex; the conformational complexities of complex formation and the dynamics of transitions between various conformations must also be considered.

We embarked on an NMR study of polyamines, including spermine, spermidine and N^1- and N^8-acetyl spermidine a few years ago and have now completely assigned all ^1H and ^{13}C resonances of the above compounds by a combination of pH-titration, decoupling and 2D-Hetcor experiments. We began this work with the goal to determine any physical chemical differences between the two isomeric acetyl spermidines that could account for their different physiological functions. The N^8-acetyl spermidine occurs in cell nuclei associated with DNA whereas the N^1-acetyl compound is an intermediate in the breakdown of spermidine and is found primarily in the cytoplasm. Even at 500 MHz the ^1H methylene resonances of spermidine and N^1-acetyl spermidine are poorly resolved with several overlapping at pH 7.5. But the chemical shifts are pH dependent and a complete assignment of all resonance was accomplished by examining spectra at pH values above and below the pH where individual resonances begin to overlap.

The NMR spectrum of spermidine alone has narrow lines characteristic of small molecules and the addition of heterogeneous calf thymus DNA causes only minute differences in the chemical shifts and linewidths of the polyamine.[1] This surprising observation has since been confirmed for spermine-d(CGCGAATTCGCG) complexes by others.[2] Apparently the bulk of polyamine binding is to sites that do not tether the polyamine down so that the polyamine in the compex has a mobility relatively unconstrained by its strong electrostatic interaction with DNA. Does this rule out the use of NMR as a method for studying this important interaction? We would like to share with you two NMR strategies we have adopted for studying this interaction.

The binding of low concentrations of certain paramagnetic ions appears to be base-sequence specific, in that some aromatic and deoxyribose ^1H resonances are broadened much more than others. This affords us an opportunity to study the competitive binding of polyamines to nucleic acids.

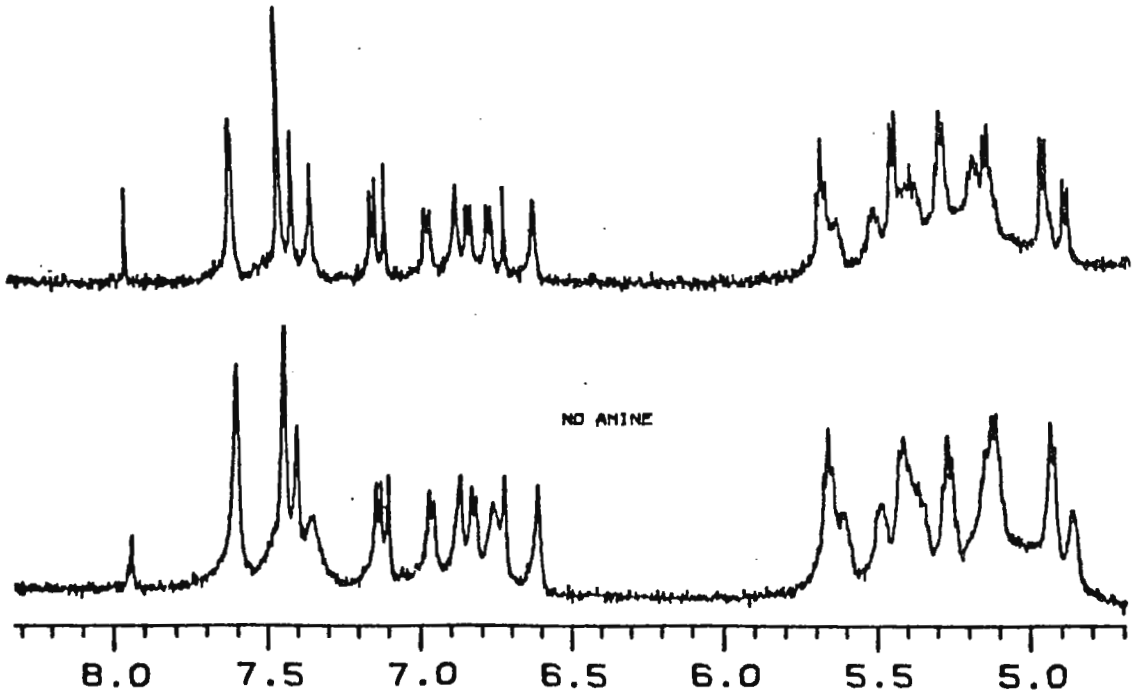
The figure illustrates that polyamines replace these paramagnetic ions and that one can monitor the relative binding of the polyamine and paramagnetic ion by studying the linewidth of the broadened DNA resonances as a function of the ratio of these two ions. The bottom spectrum of the aromatic and H_1'-resonances of ds(CGCGAATTCGCG) reveals selective broadening of the C_3G_4 resonances. In the presence of one equivalent of added polyamine (N^8-acetyl spermidine) the paramagnetic ion is displaced and the top spectrum looks exactly like that observed in the absence of added ions. This is an important and heretofore unexplored approach since low levels of polyamines by themselves provoke very little changes in the NMR of dilute dsDNA samples and their association with specific bases is hard to assess.

We have also found that polyamines cause a marked broadening of the aromatic and sugar ^1H resonances of partially thermally denatured DNA probably by shifting the ssDNA $\leftrightarrow$ dsDNA equilibrium. In a related variable temperature study of the Watson-Crick imino protons of ds(CGCGAATTCGCG) in 90% H_2O at 500 MHz, we found that polyamines increase the proton exchange rate of the outermost GC base pair while paradoxically increasing the oligonucleotide "melting temperature."

1. M. J. Minch, J. Blankenship and H. D. Pham, "Interaction of Acetylated Polyamines with DNA," ACS 20th Western Regional Meeting, Sacramento, Oct 11-12, 1984.

2. D. E. Wemmer, K. S. Srivenugopal, Brian Reid and D. Morris, J. Mol. Biol., *185*, 457-459 (1985).

top spectrum:
CGCGAATTCGCG + paramagnetic ion +N^8-acetylspermidine
bottom spectrum:
CGCGAATTCGCG + paramagnetic ion



UNIVERSITY OF CALIFORNIA, SAN FRANCISCO

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO SANTA BARBARA • SANTA CRUZ

University of California Service
Veterans Administration Medical Center
4150 Clement Street (11D)
San Francisco, California 94121
(415) 750-2146

February 16, 1988
(received 2/27/88)

Dr. Bernard L. Shapiro
TAMU NMR News Letter
966 Elsinore Court
Palo Alto, CA 94303

Re: Intensity and Phasing Standards for In Vivo MRS

Dear Dr. Shapiro:

The overall goal of research at the Magnetic Resonance Unit, Veterans Administration Medical Center, the University of California at San Francisco, continues to be development and utilization of magnetic resonance spectroscopy techniques for the investigation of intact tissues in animals and human subjects. Current instrumentation includes a Philips 2.0 T whole body magnetic resonance imaging/spectroscopy system which permits MRS from isolated volumes of interest in human tissues including brain, heart, liver, kidney, muscle and various tumors. Until recently, the major localization method which has been used is the ISIS technique (1,2). We have incorporated a post-acquisition saturation sequence into ISIS to enable its application with surface coils (3).

Absolute quantitation of phosphorus metabolite levels is of obvious importance, and our initial approach in human studies has been to make use of an intensity standard consisting of a small glass vial containing hexamethylphosphorous triamide, or HMPT ($P[N(CH_3)_2]_3$), fixed near the center of the loop of the probe. The chemical shift of this compound is well outside the range of tissue metabolites so it can be examined separately from the tissue.

Although the HMPT phantom is external to the subject, and thus the volume being shimmed, the field homogeneity at the site of the phantom is reasonably good. The phantom serves a number of purposes: first, it is visible on the proton image, enabling the coil position to be referenced with respect to anatomical features of the subject. Second, the phantom enables a pulse length determination to be made for the loaded coil (the length for a 180 pulse is determined on the phantom, and computer generated B_1 isocontour plots of the probe are used to re-scale this value for a 90^o pulse length at the center of the volume of interest (VOI)). Finally, the phantom is used as an intensity standard. Then, in a separate experiment, using a VOI identical to that used in the human study, the signal intensity of the phantom is related to that observed in a standard phosphate solution of known phosphate concentration (4). In addition, corrections for partial saturation of metabolite resonances (T_1) in human studies are required for absolute quantitation (5). In experiments with surface coils (severe B_1 inhomogeneity) the spatial shift of the VOI that accompanies chemically shifted resonances (2,3) results in altered resonance intensities due to the spatial sensitivity of the surface coil. Computer simulations are used to obtain an average sensitivity over the selected VOI, to facilitate quantitation of metabolites (5).

Signal intensities are obtained through integration of deconvoluted peaks as accomplished with the curve fit routine in the NMR-1 software (George Levy, Syracuse University). However, with spectra of poor signal-to-noise, the proper phasing can be ambiguous, and different individuals may choose different phase parameters, resulting in alterations in peak positions and intensities. To combat this phase uncertainty, we have begun using a second phantom, triphenoxyphosphine, which resonates 16 ppm downfield from HMPT. By positioning the carrier between the two phantom resonance positions and phasing both peaks, phase parameters can be obtained and applied to the human spectra that are virtually operator-independent. This procedure does require that the probe Q be sufficiently low so that the spectrometer response is not altered by the change in carrier frequency. The strong inductive coupling to the sample in our human spectroscopy experiments insures that this condition is well met.

We have recently implemented 3-dimensional phase encoding spectroscopic imaging techniques on the Philips system. Acceptable quality ^{31}P spectra have been obtained from human brain, liver, heart, and kidney. This approach is advantageous compared to "single point" MRS techniques in that metabolic information is obtained simultaneously from multiple voxels over the entire tissue region of interest.

A 7.0 T, 18 cm horizontal bore magnet system fully equipped with self-shielding gradient coils, and spectroscopy and imaging software will be delivered this summer. This system will be used for technique development, and studies of intact animals, perfused organs, and isolated cells.

Finally, we note that three recent additions to our laboratory have interests in proton spectroscopy: Drs. Andrew Maudsley (spectroscopic imaging), Hoby Hetherington (proton editing techniques), and Albert Thomas (multiple quantum studies). We hope to be able to report on their research activities in a future letter.

Sincerely,

MICHAEL W. WEINER GERALD B. MATSON BRUNO HUBESCH

DIETER J. MEYERHOFF KLAUS ROTH GREGORY S. KARCZMAR

DONALD B. TWIEG

References:

1. *Ordidge RJ, Connelly A, and Lohman JAB: J Magn Reson 66:283, 1986.*
2. *Segebarth C, Baleriaux D, Arnold DL, Luyten PR, and den Hollander JA: Radiology 165:215, 1987.*
3. *Matson GB, Twieg DB, Karczmar GS, Lawry TJ, Gober JR, Valenza M, Boska MD, and Weiner MW: Radiology (Submitted).*
4. *Roth K, Hubesch B, Meyerhoff DJ, Naruse S, Gober JR, Lawry TJ, Boska MD, Matson GB, and Weiner MW: (Submitted); Meyerhoff DJ, Karczmar GS, Matson GB, Boska MD, and Weiner MW (Submitted).*
5. *Lawry TJ, Karczmar GS, Weiner MW, and Matson GB: (Submitted).*

Telephone (0223) 337733 DEPARTMENT OF PHYSICAL CHEMISTRY UNIVERSITY OF CAMBRIDGE LENSFIELD ROAD CAMBRIDGE CB2 1EP

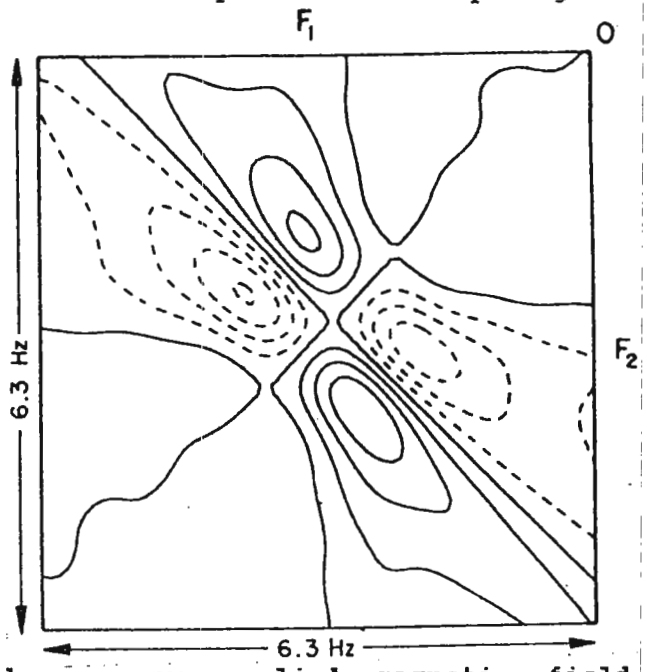
Dear Barry

A BIZARRE LINESHAPE

This comes under the heading of "partial mysteries", beloved of the early contributors to your Newsletter. It could all turn out to be wrong because it has not been substantiated by experiment.

We recently had occasion to try some 3D correlation spectroscopy by an unorthodox method involving line-selective pulses (rather than evolution and Fourier transformation). The 3D frequency space was explored with two variable frequencies F_1 and F_2, the third dimension (F_3) being examined in the usual manner by transforming a free induction signal $S(t_3)$. The selective pulses were shaped according to the first half of a Gaussian curve (1,2). They were applied (simultaneously) to an I transition and an S transition of a scalar-coupled three-spin (ISR) system. Coherence transfer to R involves the creation of IS multiple-quantum coherence - zero-quantum if the I and S transitions are regressively connected, double-quantum if they are progressively connected (3).

We used a density matrix treatment to calculate the intensity of coherence transferred to a given R transition, as a function of F_1 and F_2. For simplicity we neglected relaxation and spatial inhomogeneity effects, but took into account the time-domain shaping pattern of the selective pulses. For the regressive case the predicted intensity contour map came as no particular surprise; it is basically the familiar "phase-twist" lineshape which appears in several kinds of 2D experiment. In contrast, the predicted shape for the progressive case is quite unlike anything we have seen before (Figure 1).



The diagonals $\Delta F_1 = \Delta F_2$ and $\Delta F_1 = -\Delta F_2$ represent nodes of zero intensity. The contour diagram is antisymmetric with respect to reflection in one or other of these diagonals. There are four lobes of signal intensity, alternating positive-negative, and they are elongated along the direction $\Delta F_1 = -\Delta F_2$ (the condition for efficient excitation of double-quantum coherence).

Although we have observed the regressive responses experimentally the progressive responses have so far eluded detection, possibly because of mutual cancellation of the closely-spaced positive and negative regions in a spatially inhomogeneous applied magnetic field (neglected in the calculation).

Kindest regards

Ray

RAY FREEMAN

(received 2/24/88)

(1) Friedrich, Davies and Freeman, J. Magn. Reson. 75, 390 (1987).
(2) Davies, Friedrich and Freeman, J. Magn. Reson. 75, 540 (1987).
(3) Davies, Friedrich and Freeman, J. Magn. Reson. 76, (in press).

Bruker delivers.

Again.

Since its foundation in 1960, Bruker has continued to make major contributions to the field of commercial analytical instrumentation, especially NMR:
1963: World's first pulsed NMR spectrometer.
1967: World's first truly multinuclear high resolution NMR spectrometer.
1969: Introduction of Fourier transform techniques for NMR.

Since then Bruker has entered the fields of FT-IR, NMR Imaging (MRI), and in-vivo spectroscopy.

We introduced a fiberoptics link for high-speed data transfer and ultra-fast array processors for the new generation of NMR data processing systems.

Then in 1986 we introduced the first microscopy accessory for NMR.

And now Bruker announces the 600 MHz high resolution NMR spectrometer.

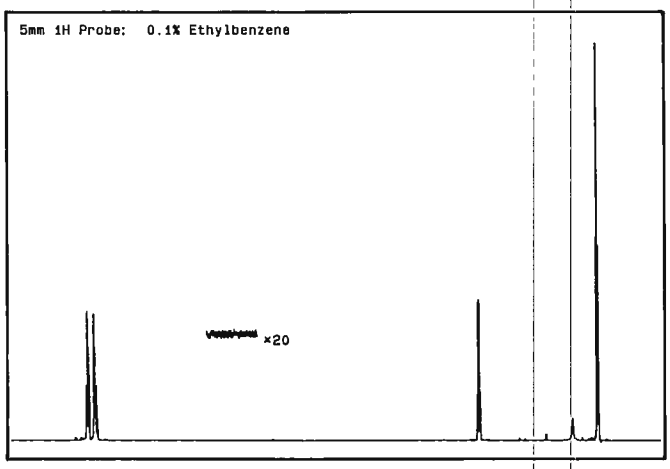
In short, no other manufacturer has advanced NMR as significantly as Bruker. And no one delivers as complete a line of systems and accessories for research and routine NMR, and as comprehensive a support package:
From hardware to software, from technical service to applications support. Bruker delivers. To find out more, drop us a line or use the reader service card.

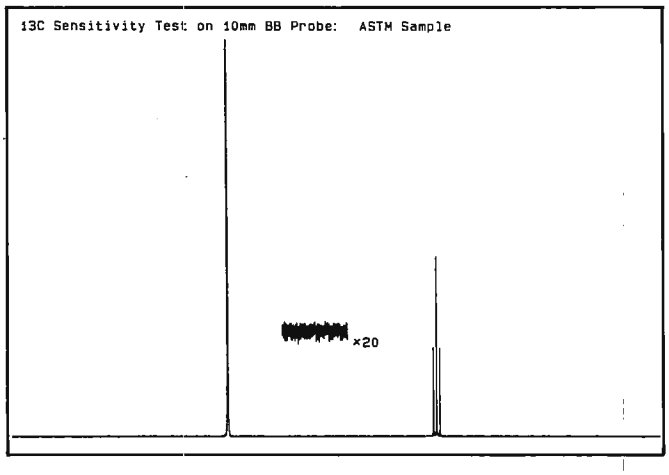
Bruker Instruments, Inc.
Manning Park, Billerica, MA 01821

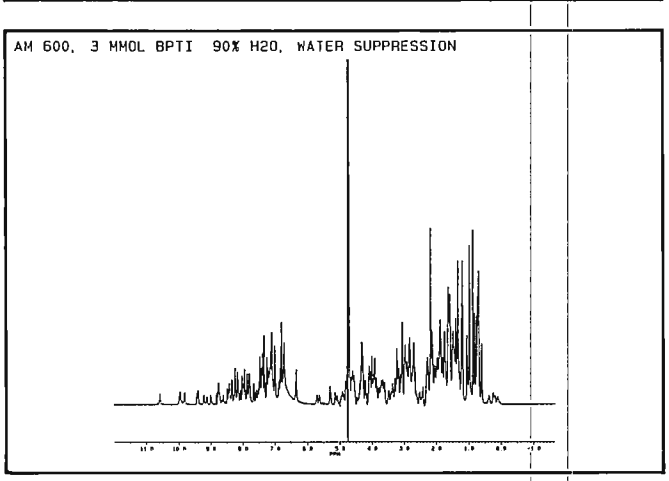
In Europe: Bruker Analytische Messtechnik GmbH, Silberstreifen, D-7512 Rheinstetten 4, W. Germany

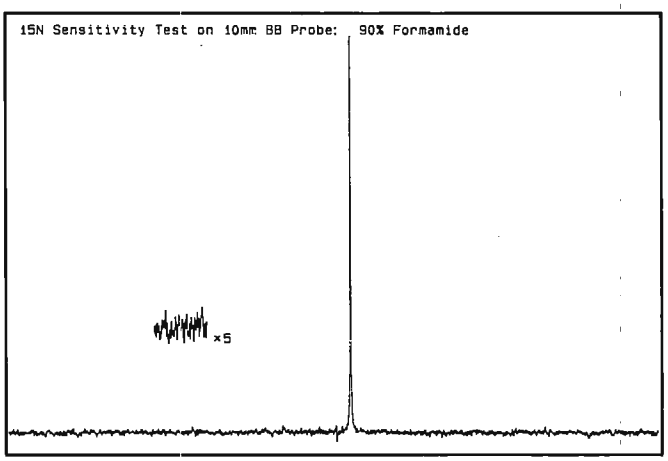
BRUKER *NMR Systems designed to solve problems.*

AM 600 NMR Spectra









Current AM 600 specifications (subject to change):

Probehead	Nucleus	Test	Value
^{1}H selective (5mm)	^{1}H	lineshape	10/20
		S/N	600:1
Broadband (5mm)	^{13}C	S/N (ASTM)	220:1
		S/N (10% EB)	180:1
		lineshape	6/15
	^{15}N	S/N (FORM)	25:1
Broadband (10mm)	^{13}C	S/N (ASTM)	650:1
		S/N (10% EB)	375:1
		lineshape	6/15
	^{15}N	S/N (FORM)	80:1

Resolution (all probes) 0.25 Hz

Magnet drift: ca. <40 Hz/hr

EB = ethylbenzene with ^{1}H decoupling
ASTM = 60% C_6D_6 in dioxane
FORM = Formamide (^{1}H decoupling without NOE)
LINESHAPE: ^{1}H = $CHC1_3$ linewidth at height of ^{13}C satellite/at 20% this level
^{13}C = C_6H_6 linewidth at 0.55%/0.11% of peak height

NMR FT-IR DATA SYSTEMS BRUKER NMR IMAGING EPR MS

Australia: BRUKER (Australia) Pty. Ltd., Earlwood, New South Wales, Tel. 02-5589747
Belgium: BRUKER SPECTROSPIN S.A./N.V., Bruxelles, Tel. (02) 7 36 11 38
Canada: BRUKER SPECTROSPIN LTD., East Milton, Ontario, Tel. (416) 876-4641
England: BRUKER SPECTROSPIN LTD., Coventry, Tel. (0203) 463770
France: SADIS BRUKER SPECTROSPIN SA, Wissembourg, Tel. (088) 94 98 77
India: BRUKER INDIA SCIENTIFIC Pvt. Ltd., Andheri (West), Bombay, Tel. 22 62 72 32
Italy: BRUKER SPECTROSPIN SRL, Milano, Tel. (02) 23 50 09, 2 36 40 69
Japan: BRUKER JAPAN CO. LTD., Ibaraki, Tel. 0298-52-1234
Netherlands: BRUKER SPECTROSPIN NV, Wormer, Tel. (75) 28 52 51
Scandinavia: BRUKER SPECTROSPIN AB, Åkersberga, Sweden, Tel. (07 64) 6 80 60
Spain: BRUKER ESPANOLA S.A., Madrid, Tel. 341-259-20-71
Switzerland: SPECTROSPIN AG, Fällanden, Tel. 182-59-111
W.-Germany: BRUKER ANALYTISCHE MESSTECHNIK GMBH, Rheinstetten, Tel. 0721-5161-0
BRUKER ANALYTISCHE MESSTECHNIK GMBH, Karlsruhe, Tel. 0721-5967-0
BRUKER-FRANZEN ANALYTIK GMBH, Bremen, Tel. 0421-8700-80
USA: BRUKER INSTRUMENTS, INC., Billerica, MA 01821, (617) 667-9580
Regional Offices in Chicago/IL, Wilmington/DE, Houston/TX, San Jose/CA

RESEARCH & DEVELOPMENT
Site Location: 709 Swedeland Road, King of Prussia, PA 19406-2799

Smith Kline & French Laboratories
A SMITHKLINE BECKMAN COMPANY

23. February 1988
(received 2/26/88)

Prof. Bernard Shapiro
966 Elsinore Court
Palo Alto CA 94303

NDS Terminals: Benefits for Hare Program Users Part II.

Dear Barry,

In my letter a few weeks back I reported how to enable gray scaling on the Northwest Digital GP-29 and GP-220 terminals, ending with a teaser comment that Dave Wemmer had told me that GP-220 terminals with 8-plane memory extensions could produce overlays of two different spectra (using Dennis Hare's FTNMR program). I have been corrected by Dave–but for the better! If I had read a little more of the NDS manual, I would have realized that both the GP-29 and GP-220 terminals, without the additional memory, can produce these plots. Since it is easy to do I thought it warranted a quickee second note.

On the GP-29: set planes to "combined" as before. The terminal is now set up to produce two graphics planes; normally these are combined to give gray scaling, but one can toggle between them using < *ctr* >**F1** (plane 1) and < *ctr* >**F2** (plane 2). Generate your first plot, and hit < *ctr* >F1, then type < *ctr* >F2 and generate the second plot (with the necessary FTNMR commands). Typing < *ctr* >-SHIFT-F5 OR's the planes for a nice overlay display; < *ctr* >-SHIFT-F6 AND's the two planes, which yields gray scaling.

I hope NDS and FTNMR users find these suggestions helpful; perhaps some clever users can report their own nifty findings in these pages.

Sincerely Yours,

Paul L. Weber

FTNMR is available from Hare Research Inc., 14810 216th NE, Woodinville WA 98072. NDS GP-29 and GP-220 terminals can be ordered from Northwest Digital Systems, Box 15288, Seattle WA 98115 (215)542-0014.

SK&F

Mailing Address: P.O. Box 1539, King of Prussia, PA 19406-0939 • (215) 270-4800
cable SMITHKLINE PHILADELPHIAPA telex 83-4487

UNIVERSITY OF LEICESTER
BIOLOGICAL NMR CENTRE

P.O. Box 138
Medical Sciences Building
University Road
LEICESTER LE1 9HN
Telephone:
Direct Line: (0533) 52_____
Switchboard: (0533) 522522

Prof. G. C. K. Roberts
Dr. L. Y. Lian

18th February, 1988
(received 3/2/88)

Professor Bernard L. Shapiro,
966, Elsinore Court,
Palo Alto,
CA 94303,
U.S.A.

Dear Professor Shapiro,

^{31}P NMR in Phosphate Buffer?

It is often difficult to perform phosphorus NMR of biological samples in phosphate buffer, because of the strong phosphorus signal of the buffer. It is not easy to irradiate the buffer signal in the homogated mode whilst observing ^{31}P (as in presaturation for observing ^{1}H in water) because most spectrometers do not have additional frequency synthesizers or probe configurations other than the standard ones. However, a very simple solution that we have adopted is to use composite pulses to suppress the buffer ^{31}P signal, in an analagous manner to water suppression techniques.

Figure 1 is the normally-recorded spectrum ^{31}P spectrum at 202 MHz of a complex of a protein (dihydrofolate reductase) and NADPH at about 3mM, in a 50mM inorganic phosphate buffer. The NADPH 2'-phosphate signal is at +2.4 ppm (w.r.t. external trimethylphosphate) and the pyrophosphates are at -14 and -16.2 ppm (a small amount of free NADPH present shows as a shoulder on the -14 ppm signal). Figure 2 is of the same sample using a 1331 pulse. The carrier was set on the buffer signal, a "1" pulse of 2 µsec and a "3" pulse of 6.2 µsec were used with gaps of 0.13 msec between them (the spectral width was 8000 Hz, a 90° pulse was 17 µsec). The 2'-phosphate signal is inverted with respect to the pyrophosphates, and its proximity to the carrier reduces its intensity. Obviously in this particular case buffer suppression was not crucial but it does illustrate how effective this technique can be. There was only a slight roll in the baseline, which could probably be eliminated by using a variation on the "binomial" pulse theme. No adjustment to the spectrometer hardware was required.

Please credit this contribution to Professor G.C.K. Roberts' subscription.

Yours sincerely,

L-Y. Lian J.R.P. Arnold

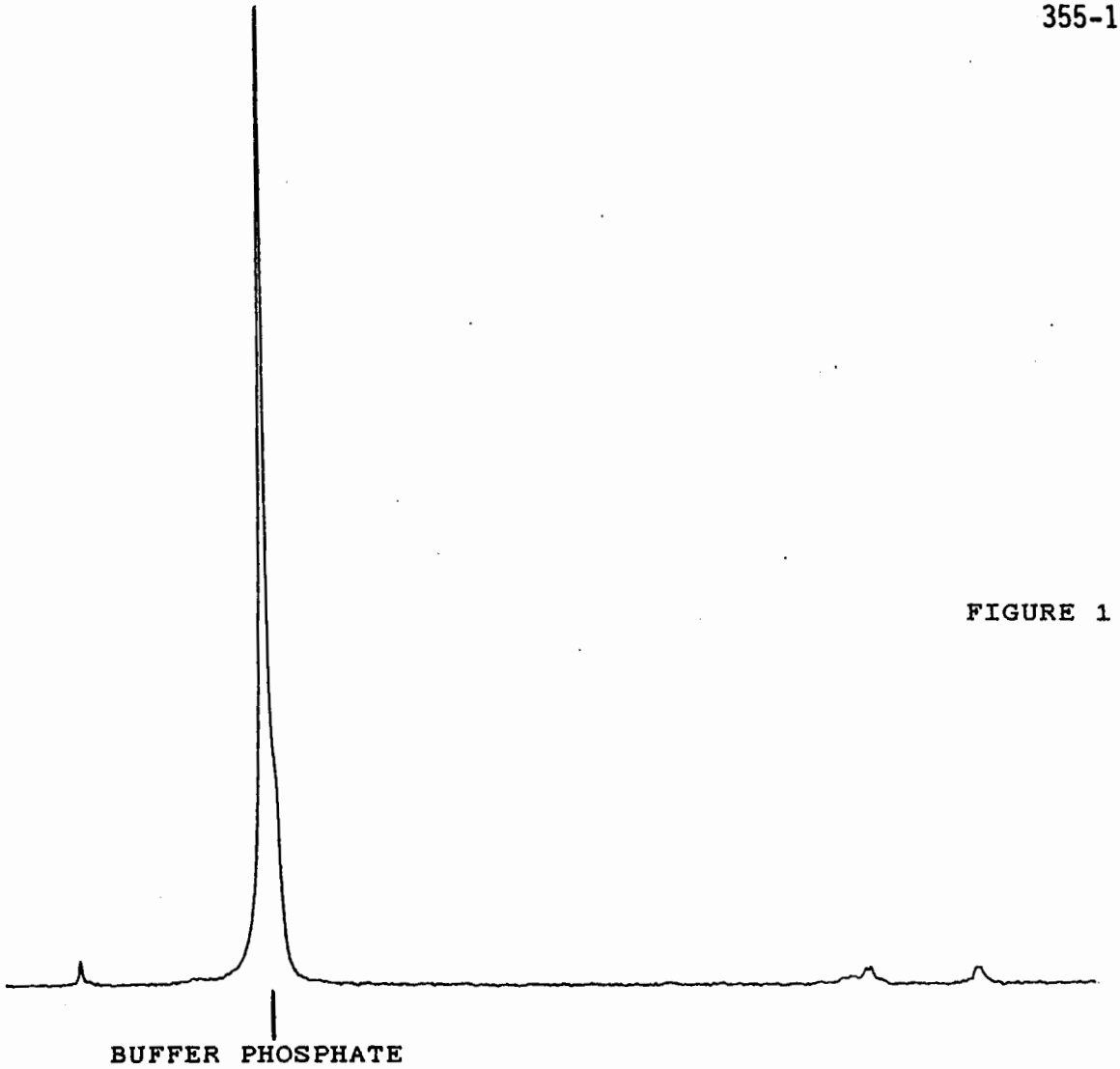
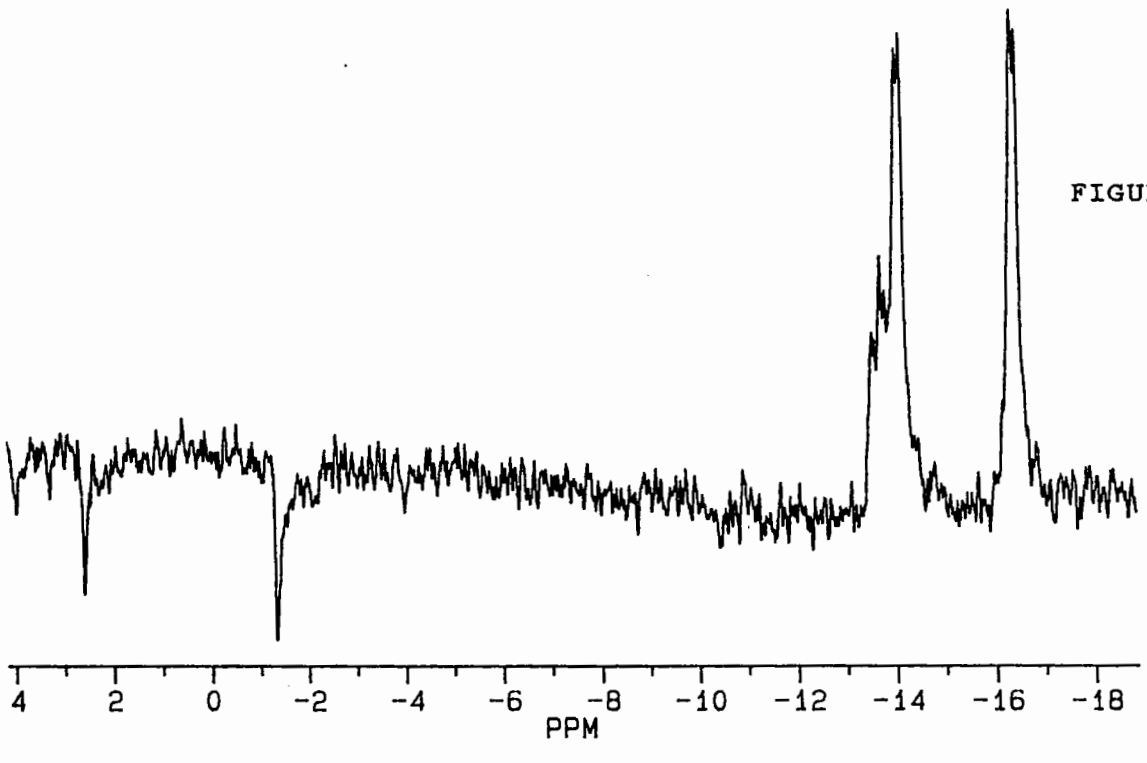


FIGURE 1



FIGURE

THE PENNSYLVANIA STATE UNIVERSITY
152 DAVEY LABORATORY
UNIVERSITY PARK, PENNSYLVANIA 16802

College of Science
Department of Chemistry

February 23, 1988
(received 2/27/88)

Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry:

LONG RANGE DIPOLAR COUPLING OF ^{13}C TO ^{14}N

We have been using ^{13}C CPMAS to characterize the solid state of molecules which can undergo the Cope rearrangement. The structure and two spectra for one of these molecules are shown on the next page.

Two hundred fifty microseconds of dead time inserted between the spin lock and the onset of decoupled acquisition causes the disappearance of all hydrogen-bearing carbons except the methyl carbons. The two cyano carbons are each split into asymmetric ugly doublets, with the larger downfield part of the doublet centered at about 125 ppm and the upfield part near 100 ppm. The splittings of the inequivalent cyano carbon resonances are caused by the dipolar coupling of ^{13}C to quadrupolar ^{14}N, which magic angle spinning is unable to completely average. The complicated powder lineshapes in each part of the doublet represent a superposition of powder lineshapes of the type described by Hexem et al.[1] The splittings, about 650 Hz, are surprisingly large for the magnetic field strength of 2.3 T, the internuclear distance of about 1.15 Å, the axial symmetry of the electric field gradient tensor, and the expected quadrupolar coupling constant of $e^2Qq/h = 3$ MHz.[1,2]

What surprised us even more, however, was the ^{13}C-^{14}N dipolar coupling apparent in the resonances of carbons 2 and 6. These are clear examples of the long-range dipolar coupling reported by Harris et al.[3] The magnitudes of the splittings and the lineshapes of these resonances are qualitatively consistent with their ^{13}C-^{14}N internuclear distances.

We hope this interesting tidbit beats your ultimatum letter. [Not quite. . . .BLS]

Regards,

Alan J. Benesi
Director, NMR Facility

and

Lloyd M. Jackman
Professor of Chemistry

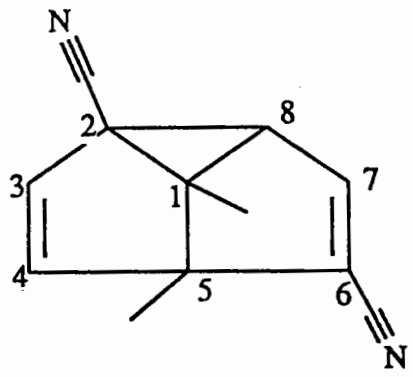
AJB/jmm

1. J. G. Hexem, M. H. Frey, and S. J. Opella, *J. Chem. Phys.*, **1982**, *77*, 3847-3856.

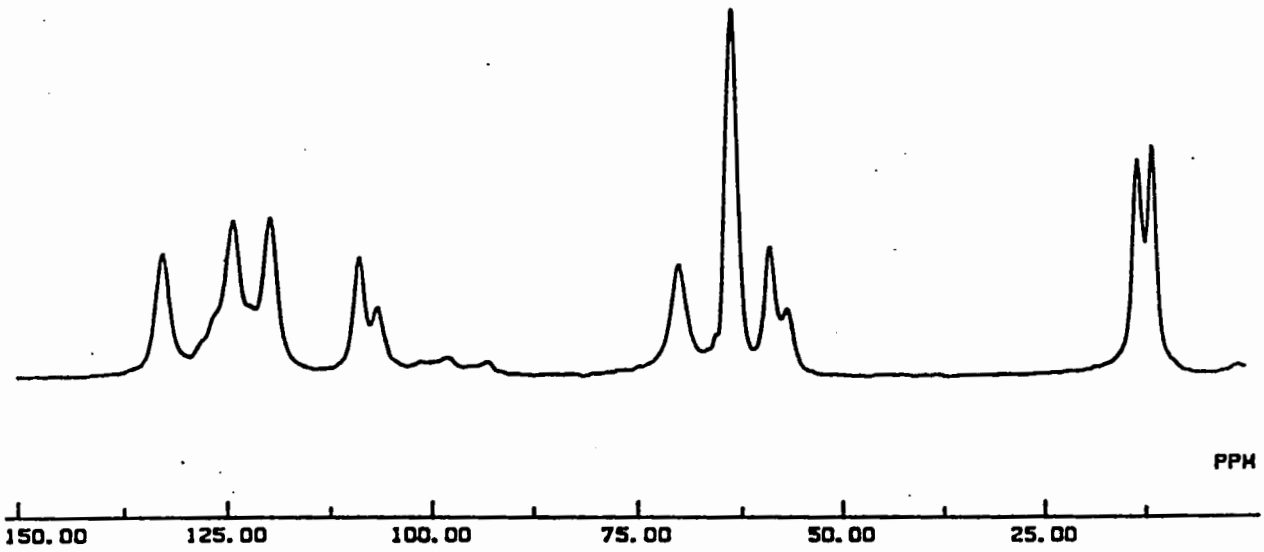
2. E. A. C. Lucken, *Nuclear Quadrupole Coupling Constants*, Academic Press, London, 1969.

3. R. K. Harris, P. Jonsen, and K. J. Packer, *Org. Magn. Reson.*, **1984**, *22*, 784.

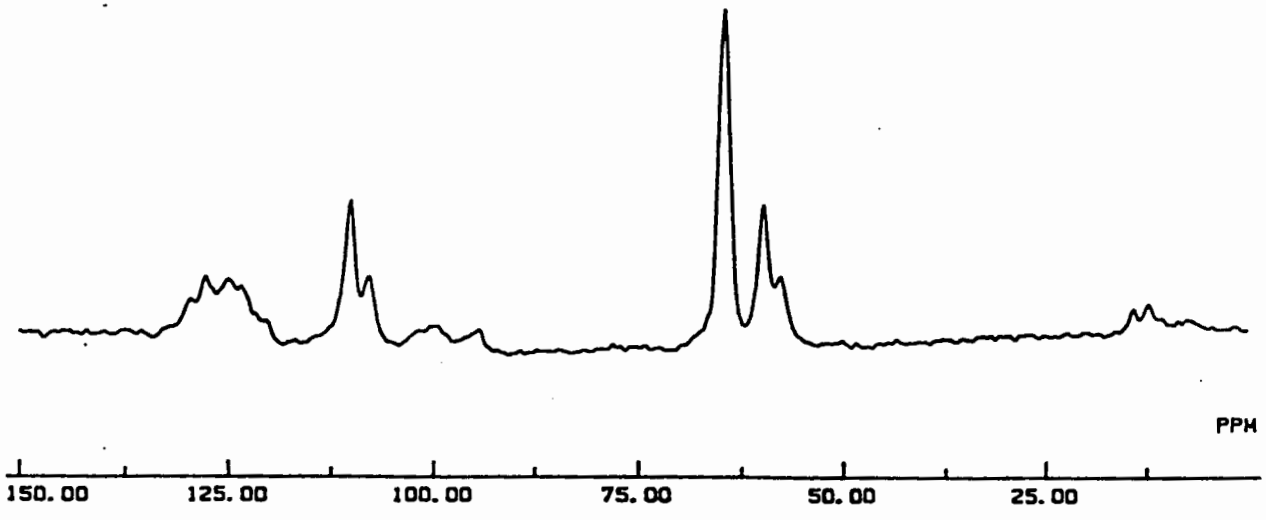
1,5-dimethyl-2,6-dicyano-semibullvalene



^{13}C CPMAS Spectrum



As above, except 250 μsec delay between spin lock and decoupled acquisition



DEPARTMENT OF HEALTH & HUMAN SERVICES
200 C St., S.W. (HFF-423)

Public Health Service

Food and Drug Administration
Washington DC 20204

March 11, 1988
(received 3/17/88)

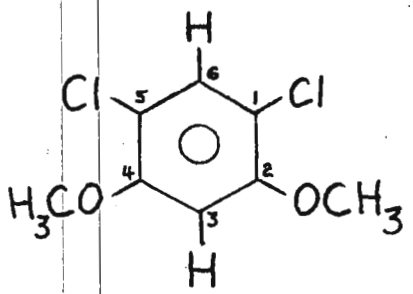
Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Ct.
Palo Alto, CA 94303

Proton Homonuclear NOE Experiments: A Practical Test Compound

Dear Barry,

Despite the sophistication of today's NMR spectrometers, it is sometimes desirable to have a compound on which one can practice NOE determinations or check instruments. This is especially the case in structural elucidation work where trans-H/H orientations may have to be inferred from the absence of NOEs. We have used several compounds as reference materials and have been particularly pleased with the following: 1,5-dichloro-2,4-dimethoxybenzene (DCDMB,1). Its proton NMR spectrum consists of single lines for the observed (H-3) and irradiated (OMe) nuclei, and there is a control nucleus (H-6) which is also a singlet. The resulting NOEs are substantial, with degassed solutions giving rise to ca. 35% enhancements in $CDCl_3$ or CS_2 at room temperature. In addition, these values appear to be unchanged at elevated temperatures and over a frequency range of 80-400 MHz.

While DCDMB is not comercially available, it can be prepared by methylating the corresponding dichlororesorcinol with dimethyl sulfate. However, a word of caution is important: dimethyl sulfate is extremely toxic and a cancer-suspect agent. Please see supplier data sheets for proper handling, i.e. wearing rubber gloves and working in a hood, and disposal procedures.



1

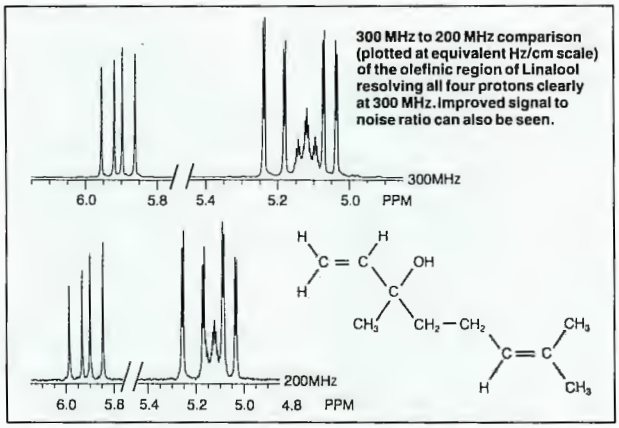
Sincerely,

Samuel W. Page

Eugene P. Mazzola

More and more labs are looking into the automated QE-300 NMR system for superior results at a price of just $160,000.

For powerful analytical insight . . . you need fast, accurate NMR results that you can interpret at a glance. With the General Electric QE-300 system you will not have to accept a compromise system that almost does the job. For the lab, a 300 MHz system can now be your minimum acceptable field strength with the best price/performance ratio.



300 MHz to 200 MHz comparison (plotted at equivalent Hz/cm scale) of the olefinic region of Linalool resolving all four protons clearly at 300 MHz. Improved signal to noise ratio can also be seen.

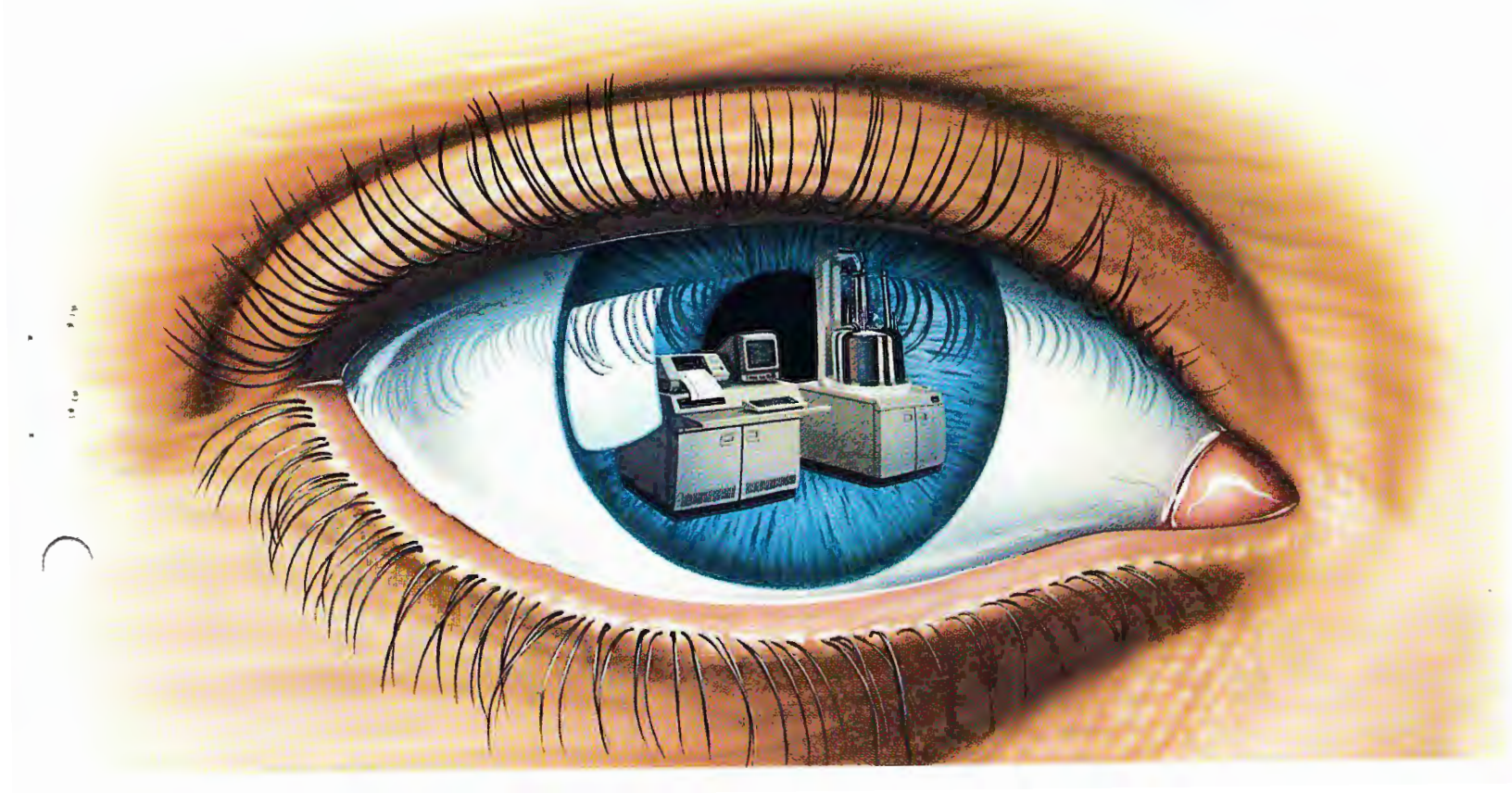
Better dispersion, faster analysis, and easier interpretation result directly from a 300 MHz superconducting magnet under the control of our custom analysis software . . . software that adapts with a few keystrokes to fit your specific analytical needs.

With the QE-300 you obtain exceptional high-resolution proton and carbon spectra from the same sample in just minutes. Plus, you have the option to observe a wide variety of other nuclei ranging from phosphorus through nitrogen. Our hardware/software options allow you to customize the system to fit your lab.

To find out what more there is to see in the QE-300 system, call (415) 490-8310 or write General Electric, NMR Instruments, 255 Fourier Avenue, Fremont, CA 94539.

See what you've been missing.

GENERAL ELECTRIC



GN Omega Series. Setting the NMR standard.

You set the specs. We created the system.

The GN Omega Series — defined by you, engineered by GE.

For the first time in the history of NMR an industry standard computer, the Sun Microsystems® workstation, has been thoroughly integrated into an NMR spectrometer.

This was accomplished without compromise to the philosophy of open architecture for both hardware and software, bringing speed *and* flexibility to the user in one package.

The system includes some exciting new GN features as well, like a new 16-bit, 200 kHz ADC with onboard memory, the Alpha HDR.

And, if you are a current GN user, ask us about our upgrade program to add Omega to your present NMR spectrometer.

The GN Omega Series — backed by GE quality, reliability and toll-free telephone support. For information or a demonstration, call (415) 683-4406 or write to GE NMR Instruments, 255 Fourier Ave., Fremont, CA 94539.

GE NMR Instrume

General Electric Company
P.O. Box 4905, Fremont, CA

GE NMR INSTRUMENTS

Product Design Specifications
GN Omega Series NMR Spectroscopy System

Sun Microsystem Workstation

DATA SYSTEM FEATURES

- 32-bit host computer
- Expandable host memory
- Ethernet™
- UNIX® operating system
- High speed array processor
- High level C language
- User programmable
- VME bus

SYSTEM ARCHITECTURE

- Total system integration
- Real time hardware control via 68020
- 16-bit, 200 kHz ADC with onboard expandable memory
- Open architecture for hardware/software expansion

The best performance in the industry

SOFTWARE FEATURES

- User friendly interface
- Access to UNIX programs
- Comprehensive NMR experiments
- Comprehensive data analysis
- Use commercially available NMR programs

GN Enhancements

RF CHARACTERISTICS

- Ultra stable frequency generation
- Very high pulse purity
- Broadband decoupler
- 1° phase shifting
- Experimental flexibility

GE NMR Instruments

3737 BELLAIRE BOULEVARD
HOUSTON, TEXAS

MAILING ADDRESS
P. O. BOX 481
HOUSTON, TEXAS 77001

February 24, 1988
(received 2/26/88)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Dr. Shapiro:

INSTALLATION OF SHIELDED GRADIENT COILS ON SHELL'S GE CSI-2T NMR IMAGING SPECTROMETER

We have recently installed a prototype shielded gradient set from GE NMR Instruments on our CSI-2T imaging system. The gradients, which were designed by P. Roemer and W. Edelstein at GE Corporate R&D, have an inner bore of 6" and can accommodate an RF coil up to 4.5" in diameter. The windings produce a maximum gradient of 18 G/cm with settling time on the order of 300 usec.

The fast switching times of the shielded gradients has allowed us to decrease the minimum echo time for 2D Fourier images from 13 ms to 5 ms. Typically, our minimum echo time is limited by the finite acquisition time of the echo itself. Less than 5 ms echo times are possible at the expense of digital resolution, i.e. echo times of 2 to 3 ms have been obtained at relatively larger field of views and/or smaller data acquisition buffer sizes. Shorter echoes could be obtained with faster data acquisition, for example using a Nicolet digital oscilloscope.

Due to the relatively short T2 values of fluids in rocks, a significant improvement in image quality is obtained at the shorter echo times as shown in the figure.

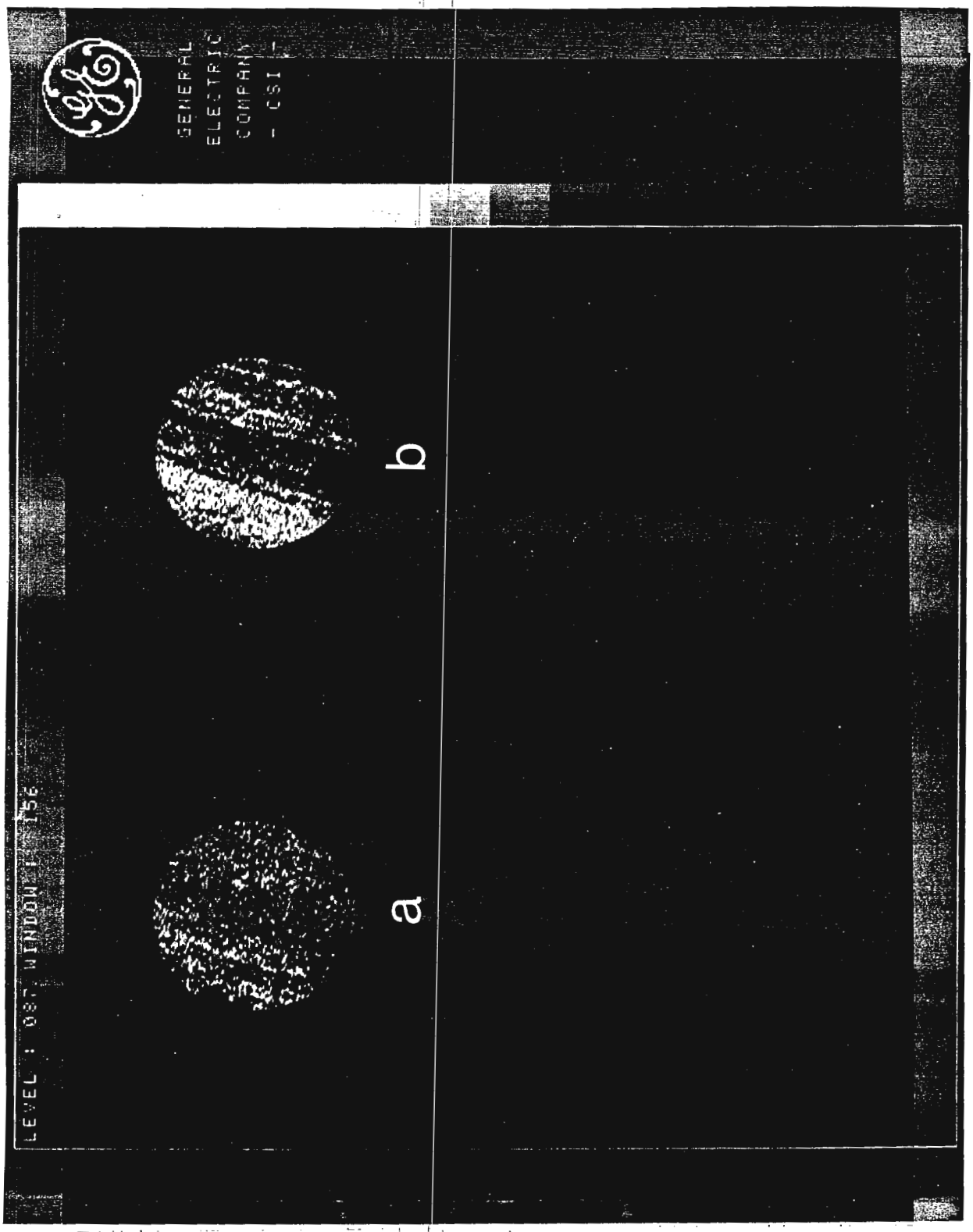
Please credit this contribution to Dr. L. L. Sterna's account.

Very truly yours,

P. N. Tutunjian
Research Chemist
Analytical Chemistry Department

H. J. Vinegar
Senior Staff Physicist
Reservoir Mechanisms Research Dept.

SHELL DEVELOPMENT COMPANY
Bellaire Research Center



2D Fourier image of a 3mm slice of Indiana limestone obtained at (a) 13 ms and (b) 5 ms echo times. The 5 ms, T2-weighted image which shows a marked improvement in image signal-to-noise clearly displays the natural bedding planes of the rock.

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue, Argonne, Illinois 60439

Telephone: (312) 972-3524

March 8, 1988
(received 3/11/88)

Dr. B. L. Shapiro
966 Elsinor Court
Palo Alto, CA 94303

RE: ^{27}Al NMR of "Aluminum-Free" Ceramic Rotors

Dear Barry:

We have been using ^{27}Al NMR to investigate the composition of clay minerals found in Argonne Premium Coals. In addition to the expected tetrahedral and octahedral ^{27}Al resonances of the clays, we observed a fairly intense signal from our Si_3Ni_4 rotor (Fig. 1). The chemical shift of 108 ppm is similar to the value reported in the literature for AlN (1). We can only assume that Al_2O_3 was used as a sintering aide during fabrication of the ceramic, even though the material was billed as being Al free. The upfield shift of 2 ppm observed from pure AlN (despite operating at the same resonance frequency) may be explained by substituting Al tetrahedra in the Si_3N_4 lattice. ^{29}Si NMR experiments performed to resolve this issue turned out to be ambiguous (Fig. 2). While the sideband intensities were unexpectedly large for ν_r = 10 kHz, the ^{29}Si linewidth was significantly sharper than that expected for a Si_3N_4 lattice substituted with Al (2). We estimate T_1 of the ^{27}Al species to be >50 s; consequently, the ^{27}Al resonance is not readily observed in spectra of pure clay samples obtained using fast pulse repetition times. However, ^{27}Al spectra of samples with little Al content, as in the case of coals, or spectra taken using longer recycle times may be dominated by this unwanted resonance.

(1) N.D. Butler, R. Dupree and M.H. Lewis, J. Mater. Sci. Lett. 3 (1984) 467.
(2) R. Dupree, M.H. Lewis, G. Leng-Ward and D.S. Williams, J. Mater. Sci. Lett. 4 (1985) 393.

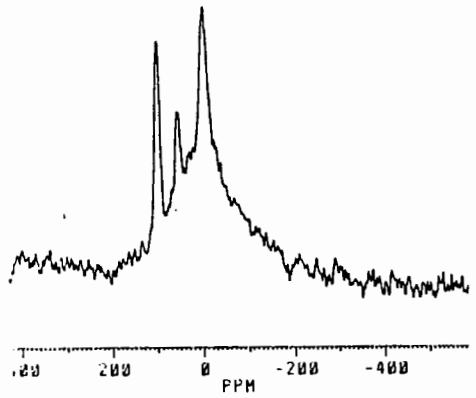


Figure 1. 78.2 MHz ^{27}Al NMR spectrum of raw coal in a "Si_3N_4" rotor spinning at 10 KHz.

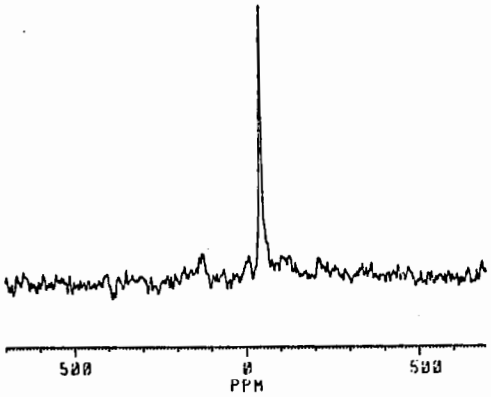


Figure 2. 59.6 MHz ^{29}Si NMR spectrum of a "Si_3N_4" rotor at 10 KHz MAS.

Sincerely,

Arthur R. Thompson
Chemistry Division

Robert E. Botto
Chemistry Division

UNIVERSITY OF STRATHCLYDE

Department of Pure and Applied Chemistry

Thomas Graham Building, 295 Cathedral Street
Glasgow G1 1XL Tel: 041-552 4400

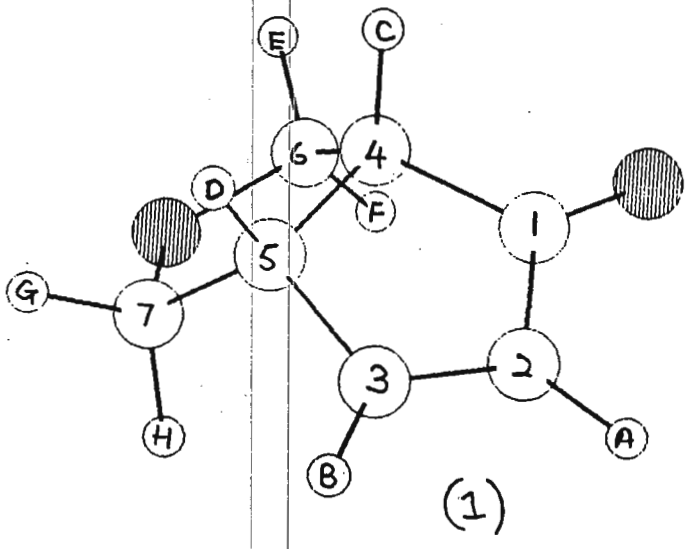
16th February, 1988
(received 3/2/88)

Dr. Bernard L. Shapiro,
Editor/Publisher TAMUNMR Newletter,
966 Elsinore Court,
Palo Alto,
California 94303.
U.S.A.

Dear Barry,

Proton and C-13 Spectra of Bicyclo-[3.3.0]-6-oxa-oct-2-ene-1-one (1).

In connection with work in this department on the use of acetylenic cobalt carbonyl complexes to form 5-membered-ring ketones (Khand reaction), it is frequently necessary to analyse in some detail the NMR spectra of intermediates. The spectra are usually nicely resolved, but sometimes there can be difficulty in assignments. The proton spectrum of the title compound forms a case in point; two of the resonances overlap and the problem was solved only by using the classical technique of selective decoupling in both the proton and carbon spectra. With regard to the carbon spectra, I feel that valuable information is gained from a proton-coupled spectrum; in this case it proved crucial in confirming the assignments.



(1)

Using the atom labels in the structure (1) the assignments are:

Proton Chemical Shifts
A 6.21; B 7.59; C 2.895; D 3.56; E 3.67;
F 4.14; G 3.66; H 3.88 ppm.

Proton Coupling Constants
AB 5.65; AD -1.65; BD 2.55; CD 6.00; CE 7.65;
CF 0.65; DG 6.95 EF -9.30; DH 0.55; GH -8.95 Hz

Carbon Chemical Shifts (multiplicity in proton-coupled spectrum)
C1 210.65 (m?); C2 135.05 (2x3); C3 164.65 (2x6); C4 49.75 (3x2);
C5 47.20 (3x2); C6 71.05 (2x4); C7 69.75 ppm. (2x2x3).

Carbon-Proton Coupling Constants (absolute values)
1-Bond couplings:
2A 172.0; 3B 165.0; 4C 138.0; 5D 140.0;
(6E+6F)/2 149.5; (7G+7H)/2 148.5 Hz.

2-Bond couplings:
6C 9.5 7D 9.0 Hz

2- and 3- Bond couplings (averaged):
(2B+2D?)/2 3.5; (3A+3D+3C?+3G?+3H?)/5 3.0;
(4E+4E+4F(/3 3.0; (5B+5C+5G+5H)/4 5.0Hz.

All experiments were made using a Bruker WM 250 machine.
Proton spectra were run at 250.13 MHz, using a spectrum width of 3000 Hz, and with 32K data points.

Carbon spectra were run at 62.9 MHz, using a spectrum width of 15000 Hz, and with 32 K data points.

Regards and Best Wishes,

Yours sincerely,

Peter

Dr. Peter Bladon

FORTHCOMING NMR MEETINGS, *continued*

Teaching Course on Nuclear Magnetic Resonance, September 5 - 9, 1988; Trondheim, Norway; Ms. I. S. Gribbestad, The MR Center, N-7034, Trondheim, Norway.

European Workshop on Nuclear Magnetic Resonance: Seminar on Contrast in MRI and MRS, September 12 - 13, 1988; Trondheim, Norway; Ms. I. S. Gribbestad, The MR Center, N-7034, Trondheim, Norway.

27th Annual Eastern Analytical Symposium and Exposition, October 2 - 7, 1988; New York Hilton Hotel, New York; General Chairman - Dr. Harvey S. Gold, Polymer Products Dept., E256/308, E. I. du Pont de Nemours & Co., Wilmington, DE 19898; (302) 695-3669.

International Post-Graduate Course 'NMR in Agriculture, Plants and Products', October 3 - 15, 1988; Wageningen, The Netherlands; Dr. Ir. J. H. de Ru, Foundation for Post-Graduate Courses, Agricultural University, Hollanseweg 1, NL-6706 KN Wageningen, The Netherlands.

Additional listings of meetings, etc., are invited.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Chemical Engineering 206-41
Pasadena, CA 91125

March 9, 1988
(received 3/11/88)

Dr. Bernard L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

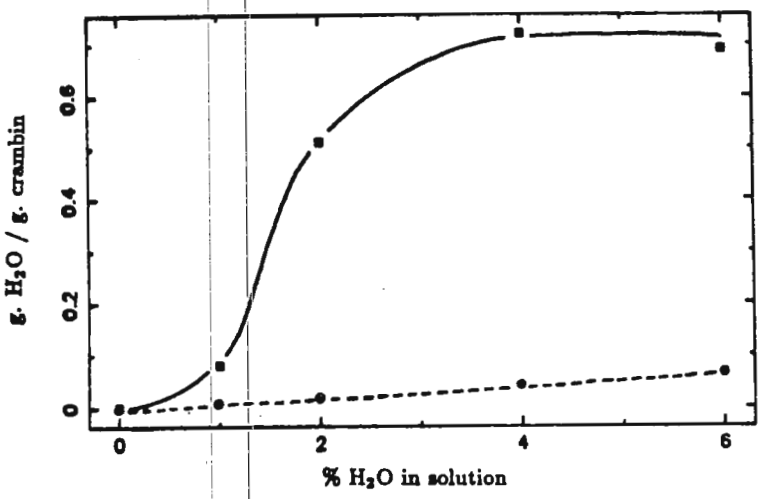
Protein Hydration by ^{17}O NMR

Dear Barry:

In order to obtain a better understanding of the role of water in affecting protein stability in nonaqueous solvents, we have studied the hydration of a hydrophobic protein, crambin, as a function of the quantity of water added to the solvent (N,N dimethylformamide). The fraction of water that is bound to the protein surface is determined by first integrating the NMR water signal at ambient temperatures (where water exists in both "bound" and "free" states), and then comparing it with the integrated intensity when the temperature is lowered to well below the freezing point of the solvent (1).

The results of our NMR studies on ^{17}O labelled H_2O (12 atom %) are shown by the solid curve in Fig. 1 for four concentrations corresponding to 1, 2, 4 and 6 percent v/v water content. The dashed curve represents the water that would be associated with the crambin if there were no selective interactions between the protein and the solvent components. It is clear that crambin exhibits a clear tendency to "extract" water to its surface in a solution that consists primarily of the nonaqueous solvent.

Further studies on protein hydration in other solvents are presently underway; it is expected that the nature of the protein hydration will provide a model that will complement current ideas concerning the role of water in enzymatic activity (2,3).



Sincerely,

Akbar Nayeem

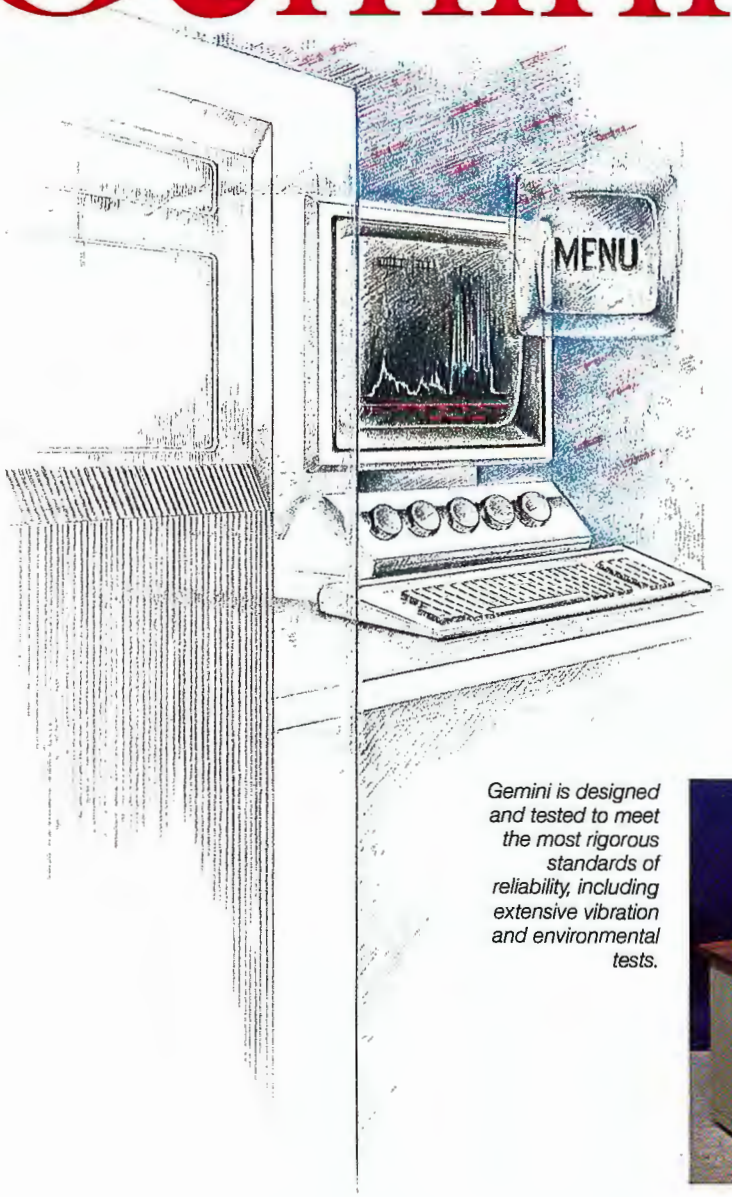
Frances Arnold

References

1. Kuntz, I. D., Brassfields, T. S., Law, G. D. and Purcell, G. V., *Science* **163**, 1329 (1969).
2. Rupley, J. A., Yang, P. H. and Tollin, G., in "*Water in Biopolymers*", ed. S. P. Rowland (Am. Chem. Soc., Washington, D.C., 1980).
3. Finney, J. L. in "*Water in Aqueous Solutions*", ed. G. W. Neilson and J. E. Enderby (Bristol, 1986).

How to acquire expert NMR data at the touch of a button

Gemini



Announcing Gemini: Never has any NMR spectrometer been this easy to learn and use

GuidePath™—our new advanced-menu user interface makes Gemini the world's easiest-to-use spectrometer. And gives you expert results!

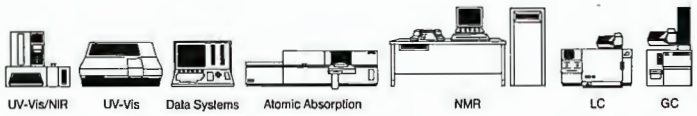
Never has FT NMR been this reliable

Gemini's industry-standard design, the complete automation of all spectrometer functions, user-proven expert system software and extensive diagnostics all combine to produce the world's most reliable FT NMR results.

Call now

Get all the facts about Gemini—the new superconducting FT NMR from Varian. In the U.S., call 800-231-5772. In Canada, call 416-457-4130. In Europe, call Zug, Switzerland, at (042) 44-88-44; Darmstadt, Germany, at (06151) 7030. In Japan, call 3-204-1211.

Gemini is designed and tested to meet the most rigorous standards of reliability, including extensive vibration and environmental tests.



INTELLIGENT SOLUTIONS FOR YOU

varian

How to bring true computer power to your NMR research

Introducing: the new VXR 5000 Series computers which integrate Varian's NMR processing and control software with computer workstations from one of the world's leading manufacturers—Sun Microsystems.*

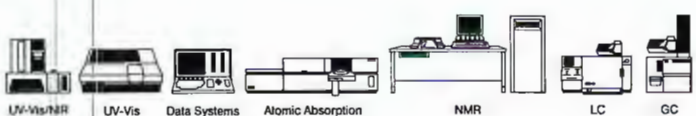
Now, for the first time, you can add a broad range of true computer capabilities to your NMR research. These features make that possible:

- **Industry-standard computers and advanced version of the UNIX* operating system**—provide high reliability and peak performance
- **Advanced windowing system**—fast and extremely easy to use
- **Flexible data processing**—from routine 1-D spectra to automatic 2-D analysis
- **Image processing**—quickly processes large, multidimensional images
- **Multipurpose and multiuser**—expands laboratory capabilities and increases productivity

The VXR 5000 series computers, standard on all our VXR and imaging spectrometers, feature a choice of monochrome or color/grayscale displays and a variety of options for enhancing performance.

Call now for all the facts
In the United States, call 800-231-5772.
In Canada, call 416-457-4130.
In Europe, call Zug, Switzerland, at (042) 44 88 44; Darmstadt, Germany, at (06151) 70 30. In Japan, call (3) 204 12 11.

*Sun Microsystems is a trademark of Sun Microsystems, Inc.
UNIX is a trademark of AT&T Bell Laboratories.



INTELLIGENT SOLUTIONS FOR YOU

varian

MAG - 4615/338

KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM
BADHUISWEG 3
1031 CM AMSTERDAM-N.
020-

Amsterdam, 2nd March 1988

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

0352

Dear Prof. Shapiro,

To my opinion NMR is one of the most fascinating fields to work in. Nevertheless it is sometimes good to change and therefore I very recently switched to a job in a completely different field. Consequently, this contribution to TAMU Newsletters will my last one. Fortunately, the NMR research at our laboratory will continue and Dr. Alex de Groot, which is also one of the authors of the present contribution, will be my successor.

I kindly request to continue our subscription to TAMU Newsletters under his name.

Finally we would like to acknowledge the contribution of Jos van Boxtel to the work presented below. Jos spent 6 months on our laboratory as a trainee of the Landbouw Universiteit Wageningen and did most of the data acquisition and processing.

A correction procedure for non-uniformities in NMR images

It is a well-known fact that NMR images may show relatively large intensity variations over the imaging plane due to non-uniform RF excitation. This non-uniformity is fully determined by the probe design and, therefore, a phenomenon we sometimes have to live with. As a consequence, quantitative comparison of the intensities of different features in an image is hindered.

In order to circumvent this problem we developed the following procedure to correct for this non-uniformity.

First, the non-uniformity itself is recorded by measuring a so-called reference image of a tube filled with water (note the variation in the intensity profile due to non-uniform excitation in Figure 1). In the second step the image manipulation software is used to "invert" the shape of the non-uniformity in order to obtain the so-called correction image (Figure 2). The procedure is illustrated in Figure 3, note that since no division of images is required, division by zero is avoided. The removal of the non-uniformity effect is demonstrated in Figure 4 where the original reference image of Figure 1 is multiplied with the correction image of Figure 3 resulting in the desired flat intensity profile.

It will be clear that once the correction image has been obtained this image can be used to correct for the non-uniformity effects in any other image by simply multiplying the image to be corrected with this correction image.

Yours sincerely,

Colette Alma Alex de Groot

N.C.M. Alma-Zeestraten and A. de Groot

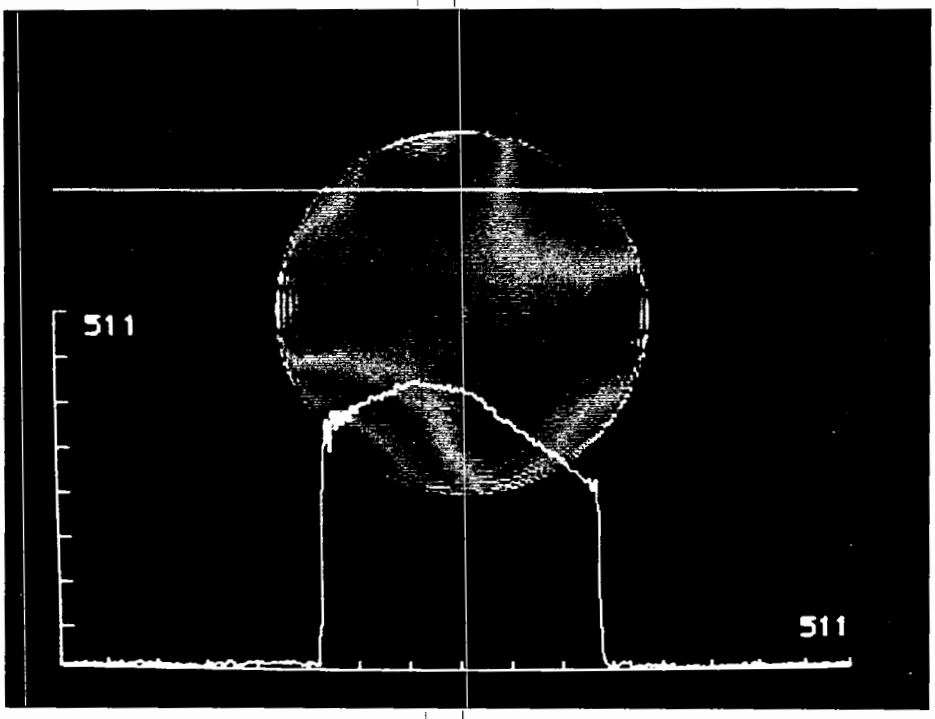


Figure 1. Image of a 30 mm diameter (maximum) tube filled with water doped with 20 mM $NiCl_2$. Clearly the intensity is non-uniform (high intensity is white, low is black). A typical intensity profile is shown (from left to right along the line across the image).

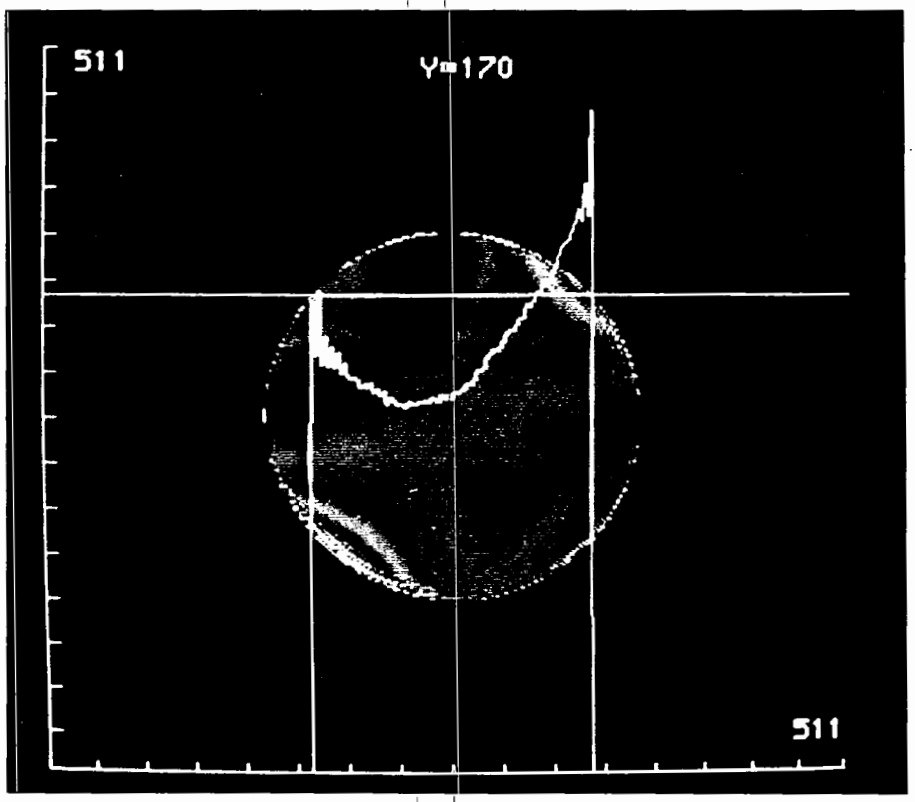


Figure 2. The correction image derived from the image in Fig. 1

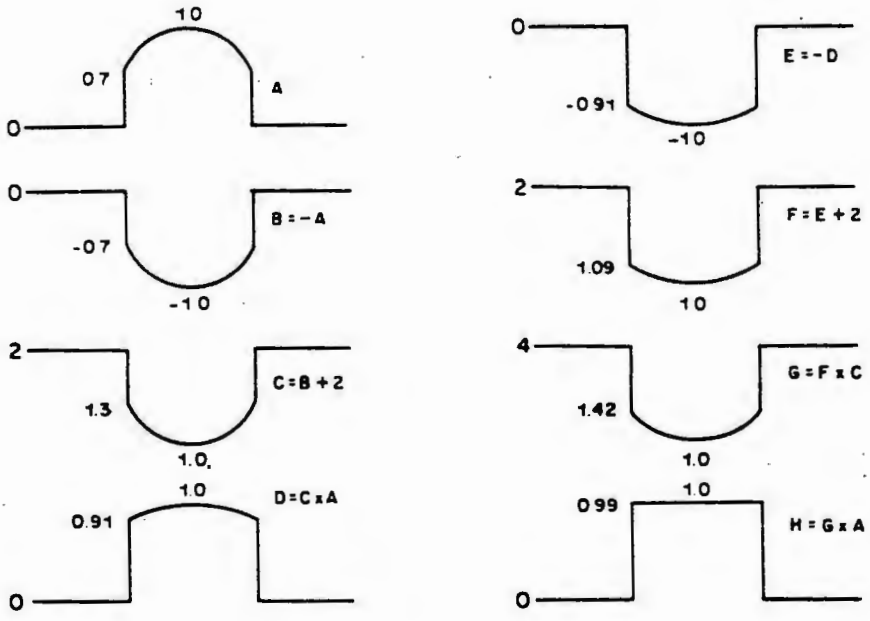


Figure 3. Schematic outline of the procedure used to derive the correction image from the reference image applied to an arbitrary intensity profile. At each step the minimum and maximum (relative) values of the intensity profile are indicated.

a. A normalized arbitrary intensity profile of the reference image (R in text)
b. Image a. multiplied by -1
c. First order correction profile
d. First order corrected profile (note that the non-uniformity is already partially removed)
e. First step for second-order correction. as b.
f. Second-order correction profile
g. Combination of first- and second-order corrections yielding the final correction profile (C in text)
h. The corrected reference profile R' (see text) obtained by multiplication of a. by g. The non-uniformity is removed.

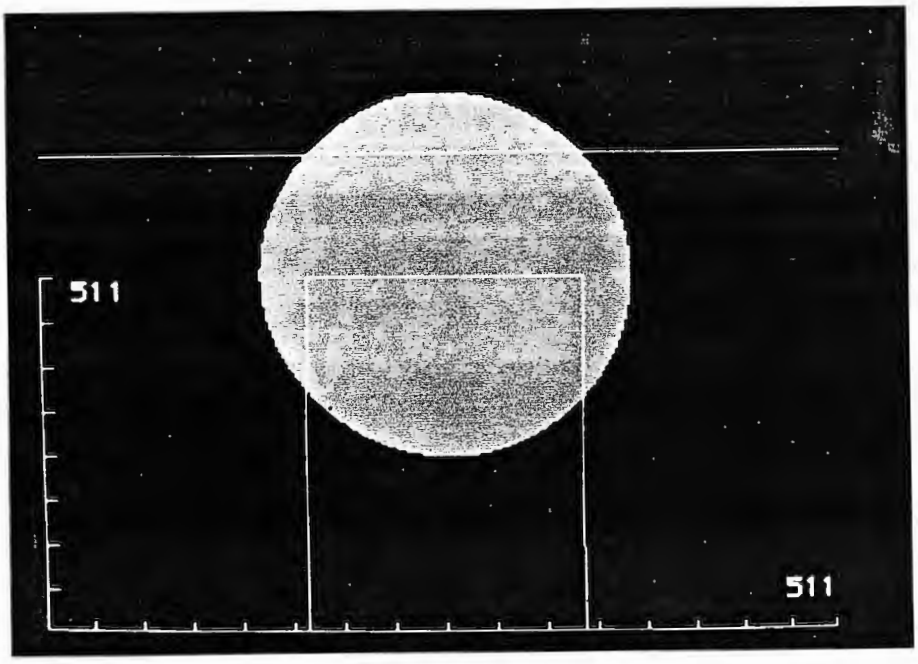


Figure 4. The corrected image.

University of Illinois
at Urbana-Champaign

School of Chemical Sciences
505 South Mathews Avenue

Urbana, IL 61801

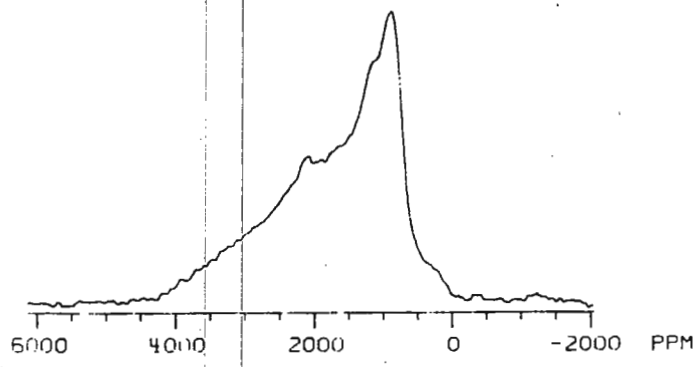
February 12, 1988
(received 3/4/88 [sic])

Dr. Bernard Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry:

Solid-State ^{17}O NMR of a Picket-Fence Porphyrin and $YBa_2Cu_3O_{7-x}$

We have recently been using ^{17}O NMR to investigate oxygen-transport proteins and model systems, both in solution and in the crystalline solid-state. The results we have obtained on $^{17}O_2$-picket fence porphyrin are shown below:

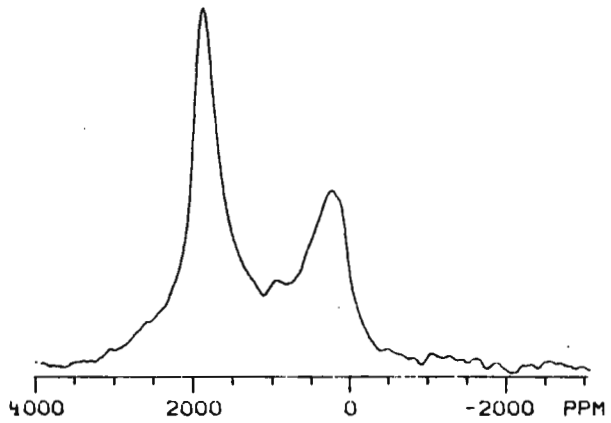


and suggest that both static and dynamic structural information can be obtained via such studies. For example, we find the isotropic chemical shifts of the bridging and terminal oxygens are at 1200 and 2000 ppm (in moderate accord with the solution results on a single-face hindered iron porphyrin-dioxygen complex of 1755 and 2488 ppm, JACS 1987, 109, 6944), that the shielding tensors are σ_{11} = 100, σ_{22} = 1200 and σ_{33} = 2400 ppm for the bridging oxygen, and σ_{11} = 850, σ_{22} = 850 and σ_{33} = 4200 ppm for the terminal oxygen, at 77 k, and that the Fe-O-O bond angle must be ~130°. Attempts of observing solid hemoglobin are underway.

We have also been investigating with Tom Rauchfuss in this Department, the ^{17}O NMR spectra of ^{17}O-labelled $YBa_2Cu_3O_{7-x}$, a high T_c superconductor. As shown in the following Figure, there appear to be two main types of (narrow) oxygen signal in the room temperature (metallic) state:

Oldfield *et allios* [sic] have herewith been declared the winners and permanent titleholders in the undeclared *Most Authors* competition, which is now closed. Forever. Please.

BLS



with isotropic shifts of ≈ 1800 and ≈ 200 ppm (from H_2O). In the superconducting state (at 77°K) there still appear to be two main sites. While these results are very preliminary, they do seem promising. T_1 measurements suggest a sizable contribution of Korringa relaxation due to the apparently large Knight shift, in the metallic state.

Yours sincerely,

E. Oldfield H. C. Lee K. D. Park E. Ramli L. Reven

T. Rauchfuss B. Montez C. Coretsopoulos L. M. Kocz[illegible]

Department of Chemistry
LOUISIANA STATE UNIVERSITY AND AGRICULTURAL AND MECHANICAL COLLEGE
BATON ROUGE · LOUISIANA · 70803-1804
504/388-3361

March 2, 1988
(received 3/5/88)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

A LabView-Controlled ADLF Spectrometer

Dear Dr. Shapiro:

We use field cycling methods, developed by Hahn and Redfield in the 1960's and later expanded by Edmonds and Brown, to acquire deuterium quadrupole coupling constants in solid samples. In the present instrument version, the sample is physically transported from high to zero magnetic fields. While the sample is in zero magnetic field, deuterium transitions are saturated with an rf field; the extent of saturation is measured through a double resonance technique that terminates with an Ostroff-Waugh experiment on the proton spin system. Then, the zero-field rf transmitter is retuned and the cycle repeated.

Because of all of the functions that must be controlled, computer programs written in traditional languages have tended to be long and complex (ca. 5000 lines of Pascal), such that only the instrument guru can make any changes. However, we recently switched to LabView, a data flow programming language that uses a block diagram approach with a graphical user interface rather than the typical sequential line coding.[1] The results have been most satisfactory. It took THREE WEEKS for two students to reprogram the instrument in LabView. Table 1 lists the main steps in the experiment. Figure 1 shows the instrument layout; figure 2 shows part of the capacitor tuning subroutine.

Table 1. Major Experiment Steps in ADLF (Mechanical Sample Motion)

- based on the 90° and 70° pulse lengths and probe ringdown times, create and load pulse program; signal averagers set to digitize 4 points at each of 128 spin echoes
- get starting parameters from front panel (starting frequency, stopping frequency, frequency increment, H_1 level, low magnetic field setting (ranges from 0 to 7 Gauss))
- initialize IEEE-488 bus and CAMAC crate controller, set zero or low magnetic field
- LOOP: frequency synthesizer, capacitors (series and parallel set according to formula and look-up table); these use BCD interfaces as does the zero magnetic field coil power supply.
- put sample in zero field coil (even at low frequency, it changes coil tuning)
- increment DAC driving variable attenuator until H_1 correct; H_1 monitored with Fluke DMM that senses current in zero field coil.
- set timing generator, signal averagers, Look-At-Me status register in CAMAC
- monitor CAMAC crate until signal averages' Look-At-Me bit set
- DMA signal averager data, calculate integral of spin echoes.
- increment frequency; if not at final frequency, then LOOP (not a GOTO but a WHILE control "statement").

Finally, I note that FORTRAN, Pascal, and Basic are older, or nearly so, than some of my graduate students. This is a weird situation for research that is, I hope, state-of-the-art.

Sincerely,

Les Butler
Assistant Professor of Inorganic Chemistry

[1] National Instruments, 12109 Technology Blvd., Austin, TX 78727-9989
(800) 531-4742

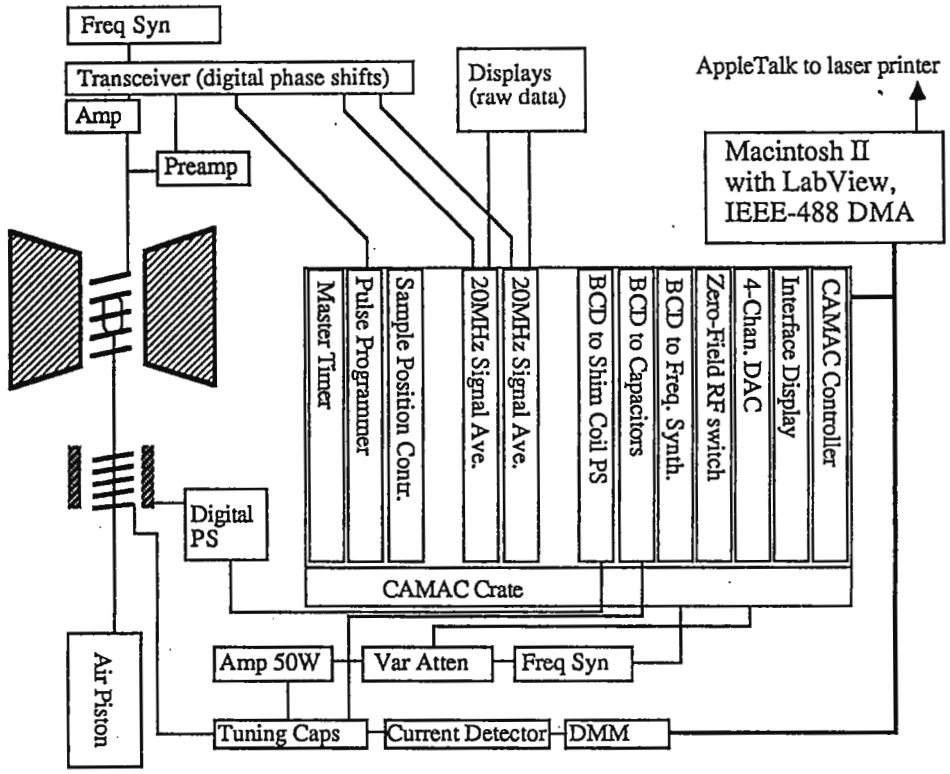


Figure 1. Layout of adiabatic demagnetization in the laboratory frame (ADLF) spectrometer; sample is mechanically shuttled between high and low magnetic fields.

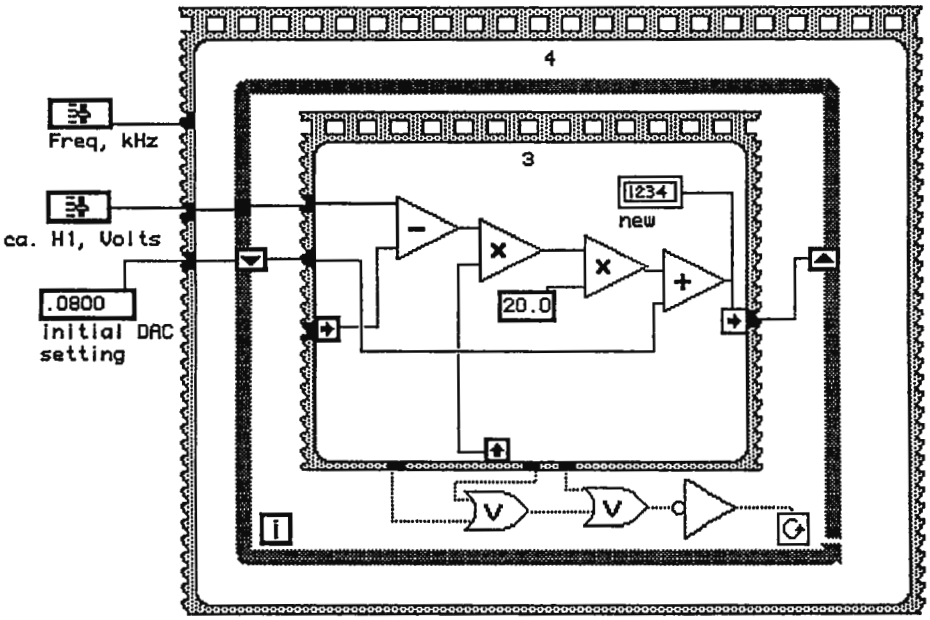


Figure 2. A portion of the H_1 tune program. In this "filmstrip", a WHILE loop will operate until the DAC driving the attenuator is set to give the desired H_1 level. The unattached input "Freq, kHz", was used in an early "filmstrip" to set the frequency synthesizer and series/parallel capacitors. The returned variable, "new", is the new DAC setting in Volts and is displayed in the front panel window in a stripchart format. This format is nice for detecting oscillations that would indicate that the gain in the "circuit", now set for 20, is too large.

(303)491-6480
Colorado State University
Fort Collins, Colorado
80523

Department of Chemistry

March 7, 1988
(received 3/10/88)

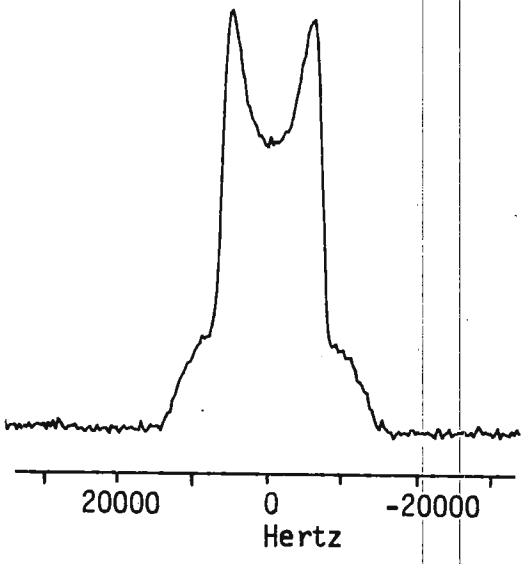
Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Ct.
Palo Alto, CA 94303

Preliminary Solid-Sample NMR Spectra on the AM-600.

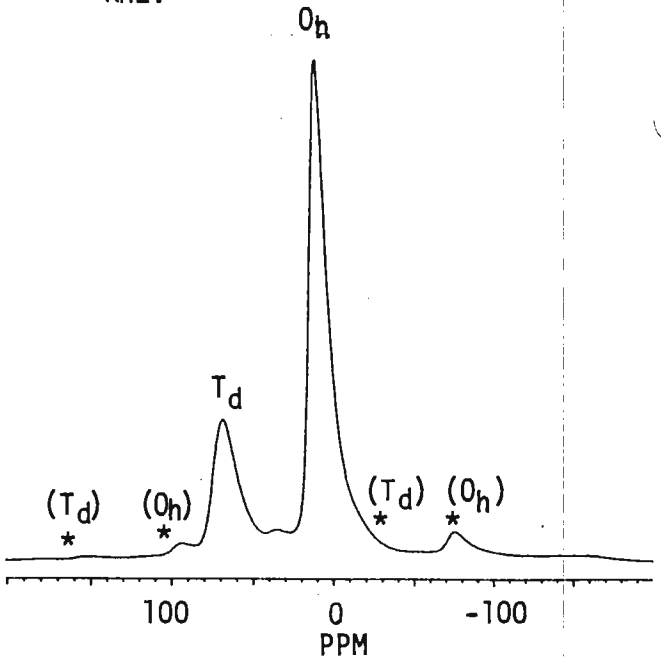
Dear Barry:

Installation of the Bruker AM-600 spectrometer in the Colorado State University Regional NMR Center has proceeded extremely smoothly. Within a few days of completion of the magnet shimming by the Bruker engineers, our laboratory (primarily Bruce Hawkins, Steve Dec and Bob Zeigler) had obtained some very promising results on solid samples. The spectra below show preliminary ^{27}Al MAS and ^{2}H spectra obtained with home-built probes.

92.1 MHz ^{2}H spectrum of silica gel derivatized with $(CD_3)_3SiCl$; with quadrupolar echo sequence.



156.4 MHz ^{27}Al spectrum of γ-alumina; with MAS at 13.1 KHz.



We are at present engaged in a vigorous and systematic program to explore what a 14 T spectrometer can do in solid-state NMR. Special emphasis is being directed to comparisons with spectra obtained on 500 MHz and 360 MHz spectrometers.

Sincerely,

Gary E. Maciel
Professor

Deuterated Solvents in Ampules
• Quality • Convenience • Variety

High-purity deuterated solvents are very hygroscopic and require careful handling to protect them from contamination by atmospheric moisture. The ideal package is the flame-sealed ampule containing the exact amount of material you require.

The following products are assayed before and after packaging to insure that ***the quality we produce is the quality you receive.*** The greatest value for your particular need can be found below in packs of 5 or 10 ampules. Ampules contain 0.5 or 1ml of solvent.

Description	1 pkg = 5 x 0.5ml Catalog No.	Price per pkg	1 pkg = 10 x 1ml Catalog No.	Price
Acetic-d_3 acid-d, 99.5 atom % D	30,869-2	$6.30	26,974-3	.5 pkg $15.00; 1 pkg $25.00
Acetone-d_6, 99.5 atom % D	30,870-6	$6.10	23,685-3	.5 pkg $10.10; 1 pkg $17.40
Acetonitrile-d_3, 99 atom % D	30,871-4	$9.75	23,686-1	.5 pkg $17.50; 1 pkg $29.30
Benzene-d_6, 99.5 atom % D	30,872-2	$7.75	23,688-8	.5 pkg $13.50; 1 pkg $22.50
Chloroform-d, 99.8 atom % D	30,873-0	$4.00	23,689-6	.5 pkg $5.30; 1 pkg $7.80
Cyclohexane-d_{12}, 99.5 atom % D	30,874-9	$41.60	26,973-5	.5 pkg $72.40; 1 pkg $120.70
Deuterium oxide, 99.8 atom % D	30,875-7	$5.00	26,979-4	.5 pkg $8.70; 1 pkg $13.10
Deuterium oxide, 99.8 atom % D (contains 0.75% 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid, sodium salt)	30,876-5	$6.30	29,838-7	.5 pkg $10.90; 1 pkg $15.20
Dichloromethane-d_2, 99.6+ atom % D	30,877-3	$28.00	23,694-2	.5 pkg $50.70; 1 pkg $84.50
***N,N*-Dimethylformamide-d_7**, 99 atom % D	30,878-1	$56.60	26,980-8	.5 pkg $107.00; 1 pkg $179.00 5 pkg $595.00
1,4-Dioxane-d_8, 98.5 atom % D	30,880-3	$37.50	26,981-6	.5 pkg $70.90; 1 pkg $117.90
Methyl-d_3 alcohol-d, 99.5 atom % D	30,881-1	$18.90	26,982-4	.5 pkg $32.70; 1 pkg $54.60
(Methyl sulfoxide)-d_6, 99.9 atom % D	30,883-8	$6.25	23,692-6	.5 pkg $10.40; 1 pkg $16.60
Nitrobenzene-d_5, 99 atom % D	30,884-6	$12.00	26,975-1	.5 pkg $34.00; 1 pkg $40.00
Nitromethane-d_3, 99 atom % D	30,885-4	$13.20	26,983-2	.5 pkg $22.00; 1 pkg $36.70
Pyridine-d_5, 99 atom % D	30,886-2	$16.70	23,695-0	.5 pkg $29.00; 1 pkg $48.50
Tetrahydrofuran-d_8, 99.5 atom % D	30,887-0	$63.40	26,984-0	.5 pkg $110.20; 1 pkg $183.70 5 pkg $609.00
Toluene-d_8, 99+ atom % D	30,888-9	$16.25	26,985-9	.5 pkg $29.40; 1 pkg $49.00
Trifluoroacetic acid-d, 99 atom % D	30,889-7	$7.25	26,977-8	.5 pkg $12.60; 1 pkg $19.90

The following *100.0 atom % D solvents are available in 0.5-ml ampules:**

Description	1 pkg = 10 x 0.5ml Catalog No.	Price
Acetone-d_6	23,696-9	.5 pkg $26.50; 1 pkg $44.50
Acetonitrile-d_3	23,701-9	.5 pkg $35.70; 1 pkg $57.50
Benzene-d_6	23,697-7	.5 pkg $29.30; 1 pkg $48.90
Chloroform-d	23,691-8	.5 pkg $11.00; 1 pkg $18.00
Deuterium oxide	26,978-6	.5 pkg $10.90; 1 pkg $16.30
Dichloromethane-d_2	23,702-7	.5 pkg $68.20; 1 pkg $113.40
(Methyl sulfoxide)-d_6	23,693-4	.5 pkg $32.60; 1 pkg $54.30
Toluene-d_8	23,703-5	.5 pkg $57.50; 1 pkg $95.90

*Minimum isotopic purity 99.96 atom % D

chemists helping chemists in research & industry
aldrich chemical co.
® P.O. Box 355, Milwaukee, Wisconsin 53201 USA • (414) 273-3850

UNIVERSITY OF CALIFORNIA, DAVIS

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO

SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

Manipulating NOEs in Paramagnetic Proteins

March 3, 1988
(received 3/8/88)

Professor B. L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

Dear Barry:

We have been interested in exploring the scope and limitations of the utility of NOEs and 2D NOESY in paramagnetic molecules for both resonance assignment and structure determination. Our emphasis has been to implement such studies on ferric enzymes such as heme peroxidases.

The major problem associated with detecting such NOEs is the strong relaxation caused by the unpaired spins of the metal which markedly decrease the magnitude of steady-state NOEs and makes it difficult to implement time-dependent NOEs.

One approach with which we have had some success is to take advantage of the fact that the correlation time for paramagnetic relaxation is usually some Orbach process which is independent of the overall motion of the system, and hence paramagnetic and diamagnetic contributions to relaxation are completely uncoupled.

This dictates that ρ, the intrinsic relaxation rate in $\eta = \sigma/\rho$, is independent of τ_c, the molecular reorientation time, while σ, the cross relaxation rate, is linearly dependent on τ_c. Thus doubling the solvent viscosity (with ethylene-glycol as solvent or addition of sucrose) should lead to a doubling of an NOE to a resonance experiencing predominantly paramagnetic relaxation. As shown in the accompanying figure for the NOEs between a pair of geminal 6-propionate α-CH_2 in high-spin ferric myoglobin, such an increase is indeed observed. In fact, the method seems to work surprisingly well.

A manuscript on the full details on the quantitative discription of such methods, as well as their limitations, is in preparation.

Best regards,

Gerd N. La Mar
Professor of Chemistry

L. B. Dugad
Research Associate

GNLM:des

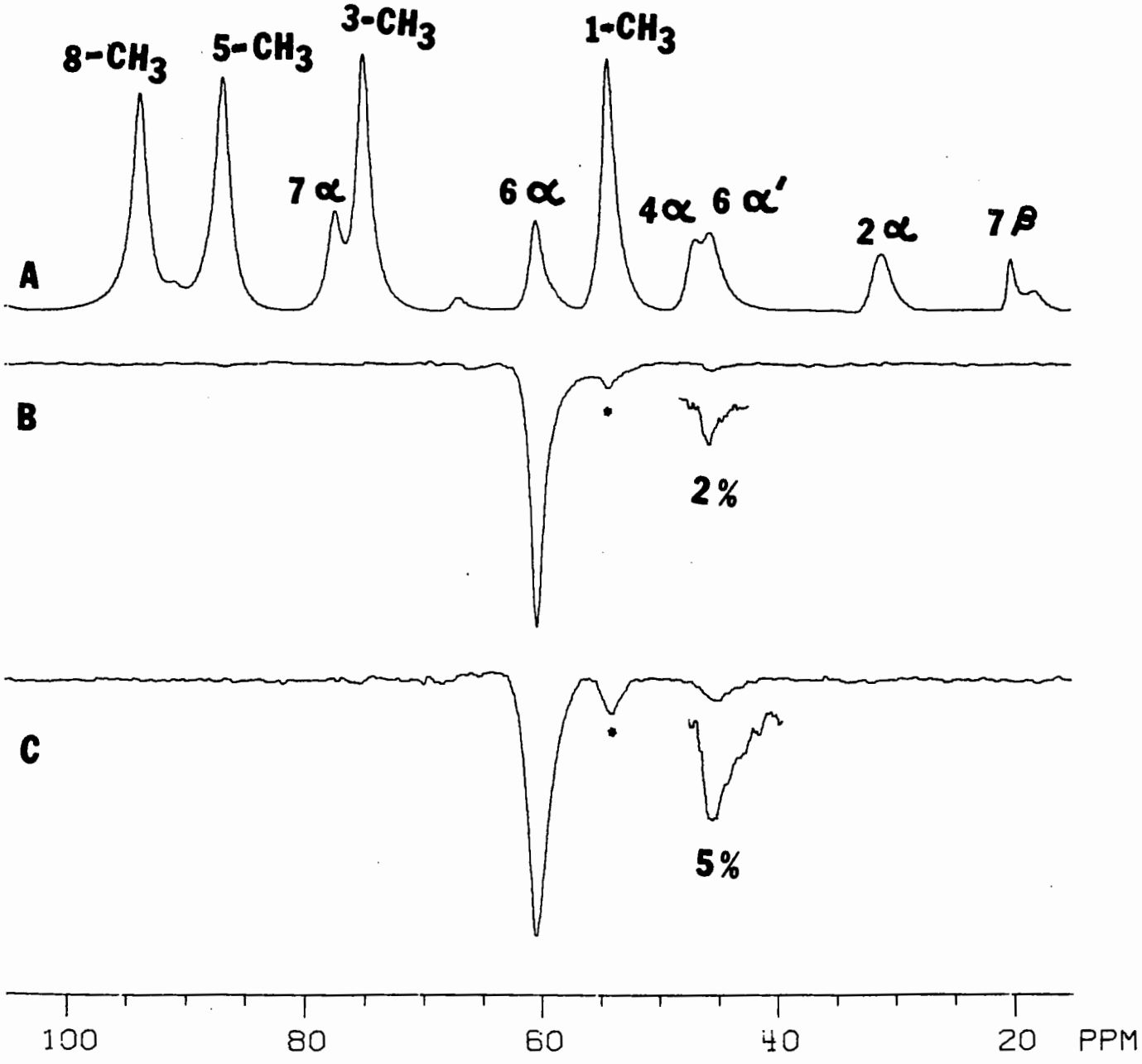


FIGURE CAPTION

Downfield region of the 360 MHz ^{1}H NMR spectrum of met-aquo myoglobin at pH 6.0, 20^{o}C. A) Reference spectrum in D_2O. B) Difference spectrum showing irradiation of 6 α proton and NOE to 6 α' in D_2O. C) Same as B but in 30% (w/w) ethylene glycol-d_6-D_2O solvent mixture. * indicates the off resonance irradiation.

PFIZER LIMITED, SANDWICH, KENT CT13 9NJ
Telephone: Sandwich (0304) 616161
Telegrams: Pfizer (Telex) Sandwich. Telex 966555
Facsimile: CCITT Groups II & III (0304) 616221

Direct line (0304)
0304-616672
February 29, 1988
(received 3/10/88)

Professor B. Shapiro,
TAMU NMR Newsletter,
966 Elsinore Court,
Palo Alto,
California 94303,
U.S.A.

Trace Analysis of Process Streams by Carbon-13 NMR

Dear Professor Shapiro,

We needed to measure low levels of two organic molecules in an aqueous wash stream. They were: $(CH_3)_3\ S^+O\ I^-$ {Trimethyl Sulphoxonium Iodide (TMSOI)} and $CH_3\ SO_3^-\ Na^+$ {Sodium Methane Sulphonate (MESNA)}.

The approximate concentrations had to be mesured quickly in order to determine whether a routine quality control assay needed to be developed. Carbon-13 NMR was selected as the analytical technique for the following reasons:

(1) Other techniques such as ion chromatography need longer development times.
(2) Little pre-treatment of aqueous samples is needed.
(3) Each compound gives a single peak in the broad-band decoupled carbon spectrum.
(4) Acquisition of spectra could be done overnight with our GE QE300 spectrometer, equipped with an autochanger.
(5) Calibration solutions are readily available.
(6) The analysis of results is quickly performed.

The carbon-13 spectra of calibration solutions of TMSOI in water /D_2O (90:10 v/v) are shown in Figures 1A to 1D. The carbon-13 spectrum of the test sample with the same concentration of D_2O added, is shown in Figure 1E. All the spectra were processed under identical conditions with the same scaling factor.

The level of TMSOI in the test sample had to be determined by extrapolating the calibration curve, because TMSOI started to crystallise from solution at a concentration of 50 mg/ml. The concentration of TMSOI in the test sample was determined as 66 mg/ml and the increased solubility is probably due to the presence of other ions in the test sample which increase the ionic strength and hence the solubility by " the salting-in" effect. The detection limit for TMSOI is less than 5 mg/ml.

The level of MESNA in the test sample was very low and no signal could be observed in the aqueous wash sample. The detection limit of MESNA was determined by a spiking experiment, which also showed that the MESNA and TMSOI peaks did not overlap at the pH used for the experiment. Figure 2A shows the carbon-13 spectrum of the test sample diluted 1:1 with water/D_2O. Figure 2B shows the test sample diluted 1:1 with a

5 mg/ml MESNA solution. The concentration of water/D_2O was 90:10 v/v in both cases. A peak at 38.5 ppm due to MESNA is separated from the TMSOI peak by 1.1 ppm in Figure 2B. The detection limit for MESNA is less than 5mg/ml.

Please credit this contribution to David V. Bowen's account.

Yours sincerely,

Pfizer Central Research

Mike Kinns Mike Newman

M. Kinns M.J.Newman.

Anaytical Chemistry Department

FIGURE 1

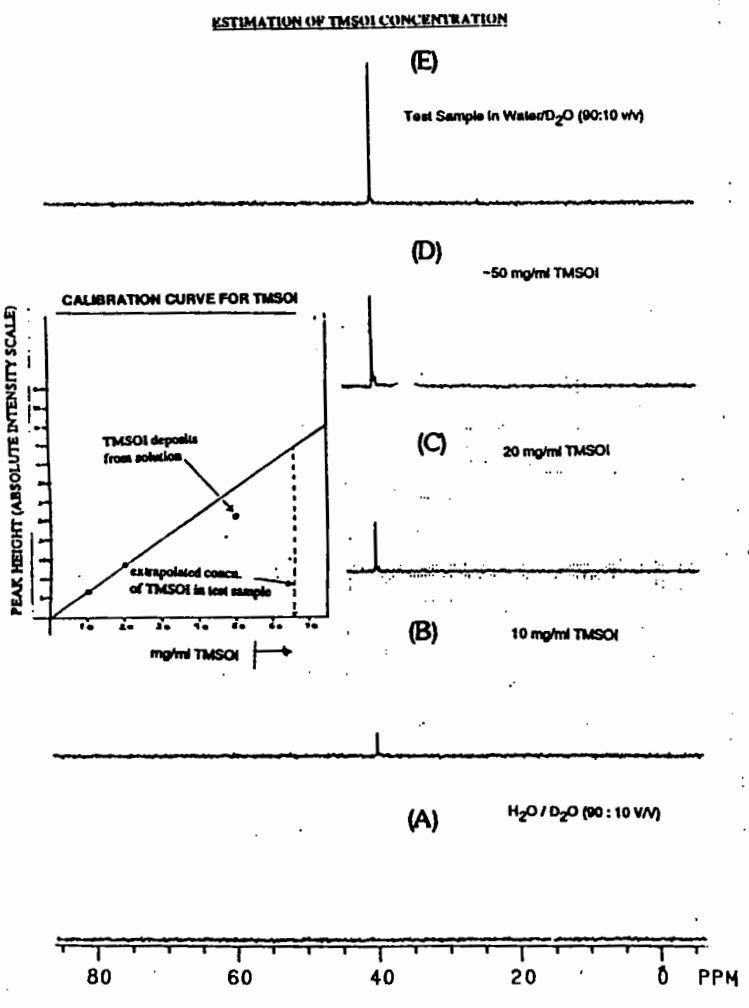
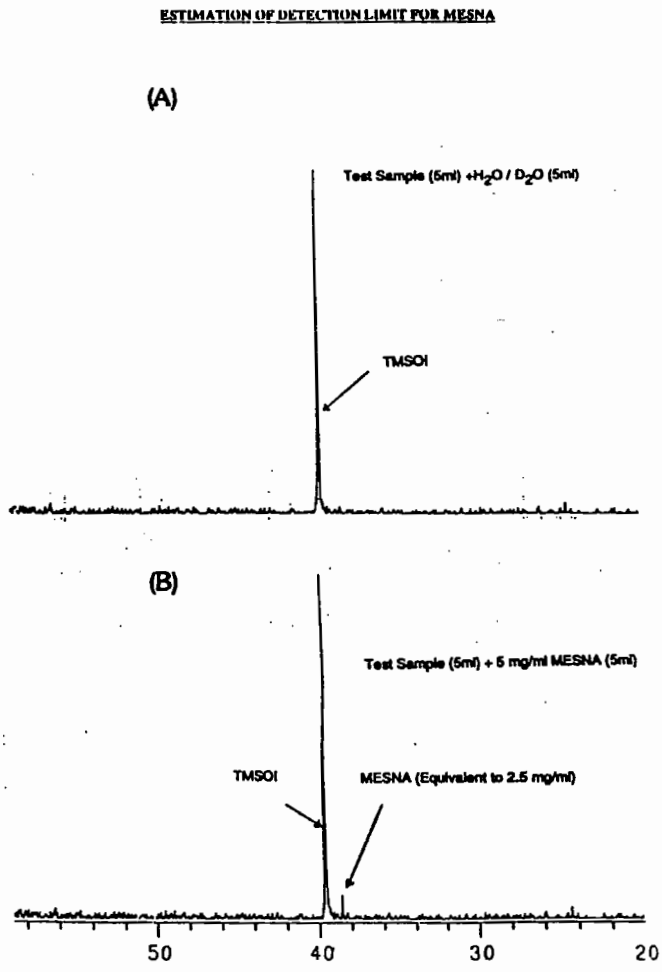


FIGURE 2



DOW CHEMICAL U.S.A.

MIDLAND, MICHIGAN 48667

March 7, 1988
(received 3/11/88)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

MAXIMUM PULSE WIDTH CRITERIA AND ENHANCEMENT RATE

Dear Barry,

It's common to try to get a semi-quantitative high resolution NMR spectrum from weak signals and as-yet-unknown components, using ordinary multiple scan single pulse experiments. I approach this from a signal/noise (S/N) "enhancement rate" viewpoint, with the goal of getting a signal fast and being confident that detected signals do not differ in degree of saturation by more than some chosen factor, such as two-fold.

One concern is reduced signal size at large frequency offset $\Delta\nu$ Hz from the pulse radiofrequency. A basic relation we are taught for 90 degree pulses in a quantitative experiment (repeat time > 3 x T_1) is $PW(90) \times \Delta\nu \leq 0.25$ to assure 99% of the zero offset signal size, where PW(90) is the 90 degree pulsewidth time in seconds. In the day-to-day world where T_1 has not been determined and we already accept partial saturation in order to raise S/N rapidly, we use pulses less than 90 degrees and would be satisfied to know that the offset is not causing more than 5 or 10 percent signal loss relative to the center position.

I have modelled the offset effect for the rapid-pulse experiment as a function of on-resonance flip angle from 0 to 90 degrees, and find as safe overall guide:

> 95% of maximum for $(PW \times \Delta\nu) < 0.3$
> 90% of maximum for $(PW \times \Delta\nu) < 0.4$.

The table below of reduced FID ENHANCEMENT RATES

$$= (\text{steady-state magnetization}) \times \sin(\text{flip angle}) \times (T_1/T_r)^{1/2}$$

illustrates this. The rate ratios and effective flip angle also are shown. The repeat time T_r is chosen to produce optimum (maximum) signals using flip angle $w(0)$ for on-resonance nuclei with longitudinal relaxation time T_1, according to the Ernst relation,

$$\cos(w(0)) = \exp(-T_{repeat}/T_1),$$

except for 90 degree flip angle where $T_r/T_1 = 1.25$ (the optimum value when $T_2^* \ll T_1$). The corresponding off-resonance flip angles $w(\Delta\nu)$ were derived from published relations (e.g. Martin, Martin, and Delpuech) and used to calculate the respective steady-state signals for the same values of T_r/T_1. The effective flip angles determined for PW x $\Delta\nu$ = 1 are less accurate because computer round-off error may be present.

REDUCED FID ENHANCEMENT RATE, S/N PER $(T_r/T_1)^{1/2}$
RAPID-SCAN CONDITIONS
T_r/T_1 is optimum for $\omega = \omega(0)$ at offset, $\Delta\nu$=0

$\omega(0)$ PW x $\Delta\nu$ =	0	.1	.25	.4	.5	1
10° Rate	.707	.707	.703	.680	.640	.000
$I(\Delta\nu)/I(0)$	1.00	1.00	.99	.96	.91	.00
$\omega(\Delta\nu)$	10	9.9	9.0	7.6	6.4	0
45° Rate	.704	.704	.698	.670	.622	.010
$I(\Delta\nu)/I(0)$	1.00	1.00	.99	.95	.88	.01
$\omega(\Delta\nu)$	45	44	40	34	28	0
70° Rate	.676	.676	.668	.629	.572	.022
$I(\Delta\nu)/I(0)$	1.00	.96	.95	.89	.81	.03
$\omega(\Delta\nu)$	70	69	62	51	42	1
90°** Rate	.638	.644	.663	.655	.611	.042
$I(\Delta\nu)/I(0)$	1.00	1.01	1.04	1.03	.96	.07
$\omega(\Delta\nu)$	90	88	79	64	52	3

** T_r/T_1 = 1.25 to maximize the net FT response for $T_2^* << T_1$.

The point is that pulse width, not flip angle per se, is the critical factor in pulse offset considerations. This point has been made many times in development of multi-pulse compensation schemes for spin inversion, etc., but is not necessarily appreciated by users at a lower level of sophistication.

Implications? Pulsewidth is a problem for rapid scanning of larger full-range spectra of nuclei such as F-19 and P-31. Pulsewidth is not a problem for C-13 on modern spectrometers. For example, at 100 MHz and maximum shift range ± 150 ppm, $\Delta\nu$ = ± 15,000 Hz, a pulse width of 27 microseconds satisfies the relation, PW x $\Delta\nu$ = 0.4; this is more than PW(90) for many spectrometers.

The run time to achieve a given FID S/N ratio is inversely proportional to the squared enhancement rate and actual time is proportional to T_1. Nuclei with different T_1 values would behave according to their own T_r/T_1 ratios and net flip angles. Remember that the minimum possible value for T_r is the data acquisition time, and that the S/N obtained after Fourier transform is maximum and proportional to T_2^* (= $1/(\pi$ x observed linewidth)) only when data acquisition time is greater than 1.5 x T_2^* (preferably 3 x T_2^*).

Jerry P. Heeschen
Analytical Sciences
Instrumental Methods
1897 Building
(517) 636-5330

lds

Weyerhaeuser Company

Tacoma, Washington 98477
(206) 924-2345

March 10, 1988
(received 3/17/88)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto CA 94303

SUBJECT: One User's Cautions on PSZ Rotors for CP/MAS NMR

Dear Dr. Shapiro:

Several months ago I switched from boron nitride to phase-stabilized zirconia as CP/MAS sample rotor body material. There are few more aggravating events than sudden decomposition of a rotor at high speed. This always seems to occur during a crucial experiment and requires a couple hours downtime to clean the probe and start over.

Over the years I have destroyed about a dozen BN rotors and except for the time loss and the need to repeat some experiments, no real damage has occurred. This spinner system is of the double-air-bearing design, with polyimide bearing surfaces at the top and bottom of the ceramic body which float in brass stator journals. When BN rotors come apart under stress, they normally break into very small pieces (powder); even though these microchunks fly everywhere inside the spinner/coil compartment, they cause no physical damage to the static components - rather like throwing handfuls of powdered sugar against the kitchen wall.

A different situation pertains to PSZ rotor bodies, however. A few months ago, I had one of these self-destruct at 3 krps and I was startled to find that PSZ breaks into larger pieces than BN and that, owing to PSZ's greater hardness and density, these pieces hit things with sufficient momentum to damage them. Besides putting dents and gouges in the rf coil, some of these particles became wedged between the rotor bearings and stator journals, digging divots in the brass journal surfaces and chewing up the bearings.

The outcome of this disaster was replacement of the entire stator assembly. Naturally, the manufacturer does not stock supplies of this item, so the spectrometer collected dust while waiting six weeks for custom engineering and manufacturing to be completed. Eventually, I succeeded in getting new journals fitted in the original stator, leaving me with a handy back-up for the next rotor explosion.

All in all, this was a costly and time-consuming chain of events. I recommend that those who use PSZ rotors keep spare stator assemblies on hand; sooner or later, this will happen to them.

Respectfully,

Larry Amos

Larry W. Amos
Analytical Laboratories
Weyerhaeuser Analytical
and Testing Services


2
9
9
MHz
9
9
9
KHz
9
9
9
LOCAL
REMOTE
CONTROL
PTS300
FREQUENCY SYNTHESIZER 1-300 MHz

The PTS 300 joins our growing line of direct synthesizers that cover 0.1 to 500 MHz. A new development that answers the demand for compact devices (3½″ rack space), it still benefits from a decade of experience and manufacturing expertise that have made PTS synthesizers the number one choice in OEM applications. With thousands in use they serve many diverse applications, including communications, ECM, mode locking, ATE and MR Imaging.

The PTS 300 is a generator of precision frequencies. It transfers the accuracy and stability of a frequency standard (built-in or external) to any output frequency between 0.1 and 300 MHz. Resolution is 1 Hz throughout the range, remote-only versions are available.

With its low spurious outputs, fast switching, low phase noise, choice of signal purity and digital phase modulation, it sets new standards in performance/price for low noise synthesized sources.

Both versions of the PTS 300 switch phase-continuously for all steps 1 Hz through 100 KHz.

The calculated MTBF of PTS synthesizers is 7,000 hours. Evaluation of service records for many thousands of units show a figure of 25,000 hours. A yearly failure rate of 3-4% is typical. Warranty is two years from date of shipment. For ease of service the PTS 300 uses plug-in modular design throughout.

PRELIMINARY SPECIFICATIONS

FREQUENCY	Range:	0.1 MHz to 300 MHz (299.999 999 MHz)	
	Resolution:	1 Hz	
	Control:	Local by 10-position switches. Remote by TTL-BCD, 1248, buffered par. entry	
	Switching Time:	20 micro-sec (10 MHz, 100 MHz steps) 5 micro-sec (1 MHz steps) 1 + 2 micro-sec, (transient + delay) for all steps 1 Hz -100 KHz); (phase continuous)	
OUTPUT	Level:	+3 to +13dBm, (1V) into 50 ohms, metered in dBm and volt	
	Flatness:	±0.5dB	
	Impedance:	50 ohms	
	Control:	Manual by F/P control, remote by voltage (+0.63 to +2.00V)	
		Type 1	**Type 2**
SPURIOUS OUTPUT	Discrete	−70/65dB (typ./spec)	−60/55dB
	Harmonics	−30dB	
	Phase Noise:	−68dBc (0.5Hz-15KHz)	−63dBc (0.5Hz-15KHz)
	Noise Floor:	−135dB/Hz	
	Phase Setting: (digital)	0°, 90°, 180°, 270° standard; 5° resolution optional 0-360°	0-360° in .225° steps optional
FREQUENCY STANDARD Int. Std. *or* ext. Drive required for operation	Internal: (OPTIONAL)	3×10^{-9}/day $\pm 1 \times 10^{-8}$/0-50°C 1×10^{-6}/year (OVEN)	or 1×10^{-8}/day $\pm 1 \times 10^{-6}$/0-50°C 2×10^{-6}/year (TCXO)
GENERAL	External Drive:	10 MHz, 0.4Vrms into 300 ohms; 5 MHz, 0.5Vrms into 300 ohms	
	Aux. Output:	10.000 MHz, 0.4V into 50 ohms	
	Oper. Ambient:	0 to 55°C, 95% R.H.	
	Power:	105-125V, 50-400 Hz, 40 Watts (100V, 220V, 240V available)	
	Dimensions/Weight:	19 × 3½ × 17″ (relay rack or bench cabinet) 25 lbs.	
PRICES (domestic)	Price: (Manual & Remote Controls, TCXO)	$5,550.00	$5,050.00

PROGRAMMED TEST SOURCES, inc.

BOX 517, LITTLETON, MA 01460 617-486-3008, 617-263-6467
FAX 617-486-4495

12/87

ETH Eidgenössische Technische Hochschule Zürich

Ecole polytechnique fédérale de Zurich
Politecnico federale di Zurigo
Swiss Federal Institute of Technology Zurich

Laboratorium für Physikalische Chemie
Prof. Dr. R.R. Ernst

Universitätsstrasse 22
Durchwahl-Nr. 01/256 43 68
Telefonzentrale 01/256 22 11

Postadresse:
Laboratorium für Physikalische Chemie
ETH-Zentrum
8092 Zürich
Switzerland

0430

Professor B.L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
PALO ALTO
California 94303 USA

Zürich, March 10, 1988
(received 3/14/88)

COMPUTER FITTING, A LAST RESORT REMEDY IN 2D SPECTROSCOPY

Dear Barry,

It is wellknown that spectra which exuberate with information are notoriously difficult to analyze. Two-dimensional correlation spectra of medium-size molecules are typical in this respect. As soon as strong coupling is present, a logical straight forward analysis by a skilled spectroscopist or by a trained computer is difficult or impossible and accurate chemical shifts and coupling values cannot be determined.

In this situation, least squares fitting is usually a last resort remedy to reach the goal. We have explored the feasibility of iterative fitting of cross-peak multiplets in 2D correlation spectra of the E.COSY-type in order to determine coupling constants and chemical shifts. The approach is similar to fitting 1D spectra. A reasonable set of initial values is chosen, and selected regions of a 2D spectrum are simulated and compared with the experimental spectrum. The parameters are then iteratively refined following one of the wellknown strategies of optimization. The error surface can also in

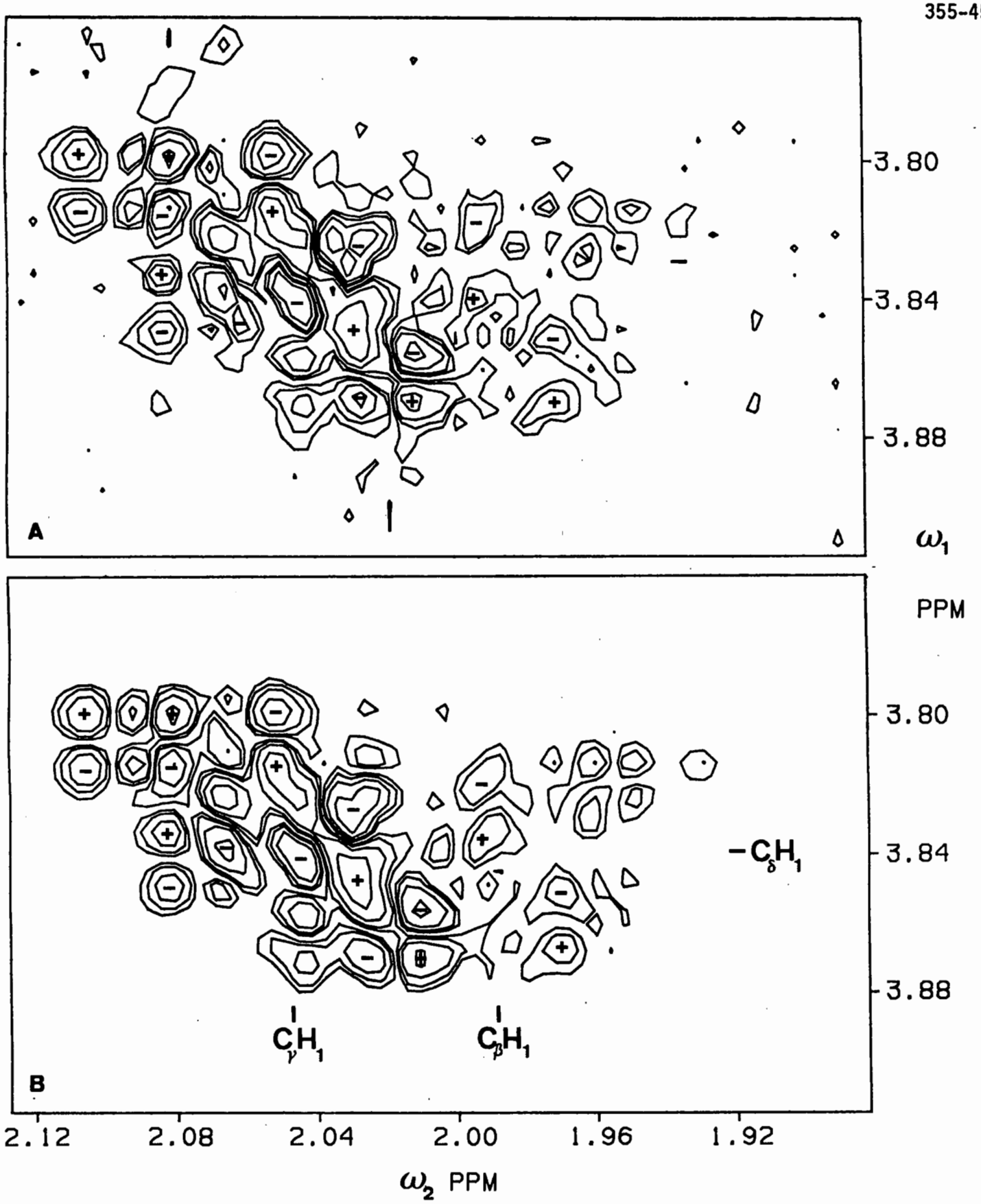
this situation be very treacherous with countless crevasses and local minima. Temporary smoothing of the error surface by peak broadening is normally indispensible.

A novice in computer fitting of 2D spectra will rapidly become disappointed by the fact that his recently acquired pocket calculator is hardly of any use and that even most powerful computers are kept busy for appreciable time before a satisfactory fit is reached. As a demsonstration example, the strongly coupled proline-2 seven-spin system in a 300 MHz E.COSY spectrum of the cyclic decapeptide antamanide has been analyzed. Two chemical shifts and six coupling constants were determined in a first step from the $C_\delta H_1$-$C_\delta H_2$ cross peak. The remaining five chemical shifts and 15 coupling constants, together with two linewidth parameters and the overall intensity were obtained from a 23 parameter fit in 14 iteration steps of the cross peaks between $C_\delta H_1$ and $C_\beta H_1$, $C_\beta H_2$, $C_\gamma H_1$ and $C_\gamma H_2$. The Modula-2 program was running for 55h 43min (!) on a DEC μVAXII-GPX computer with an ULTRIX-32w Operating system. The fit shown for the overlapping cross peaks $C_\delta H_1$-$C_\beta H_1$ and $C_\delta H_1$-$C_\gamma H_1$ is certainly as good as it can be expected and the coupling constants obtained are accurate to about 0.1 Hz. The full story is presently in print in the Journal of Magnetic Resonance.

Sincerely yours,

Zoltán L. Mádi

Richard R. Ernst



Cross-peak region from a 300 MHz E.COSY spectrum of the cyclic decapeptide antamanide containing two cross peaks of proline-2. A: experimental spectrum, B: computer fit.

UNIVERSITY of PENNSYLVANIA

School of Medicine
Department of
Biochemistry and Biophysics
Philadelphia, PA 19104-6089

February 26, 1988

Dr. Bernard L. Shapiro
Editor - TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Dr. Shapiro:

We would like to report on a resonator based on the "cosine coil" design built for NMR studies on human heads and limbs. Basically, the coil consists of linear wire segments distributed around a cylinder in a way that there is a "cosine" distribution of current leading to a very large volume of B1 homogeneity. (A detailed paper describing this coil design has just been accepted for publication: L. Bolinger et al., J. Magn. Res.)

Our head coil has been built around a 32cm polypropylene cylinder as the former (a standard distilled water carboy with its neck and bottom sawn off). The coil segments are made from 1 mil thick adhesive backed copper strips (0.7cm wide & 32cm long). On either end of the coil we have used 4cm wide copper strips as one plate of the tuning capacitor. We have fabricated two end rings also made from polypropylene to slide over the formeer. Two more 4cm wide copper strips have been glued to the end rings to form a high voltage variable capacitor. Tuning is achieved simply by sliding the end rings over the former. The self resonance frequency of this coil is over 100 MHz and with our capacitor we can tune it from 50 MHz to 90 MHz. This tuned circuit is coupled to the T/R switch inductively.

The unloaded Q of this coil is over 250 while loaded Q (with a human head inside) drops to about 100. The 90 degree pulse width on a human head at 78 MHz proton frequency is about 250 microsec with a 400W transmitter power. The B1 inhomogeneity over a human head seems to be less than 10%. A simplified diagram of this coil is given in the figure.

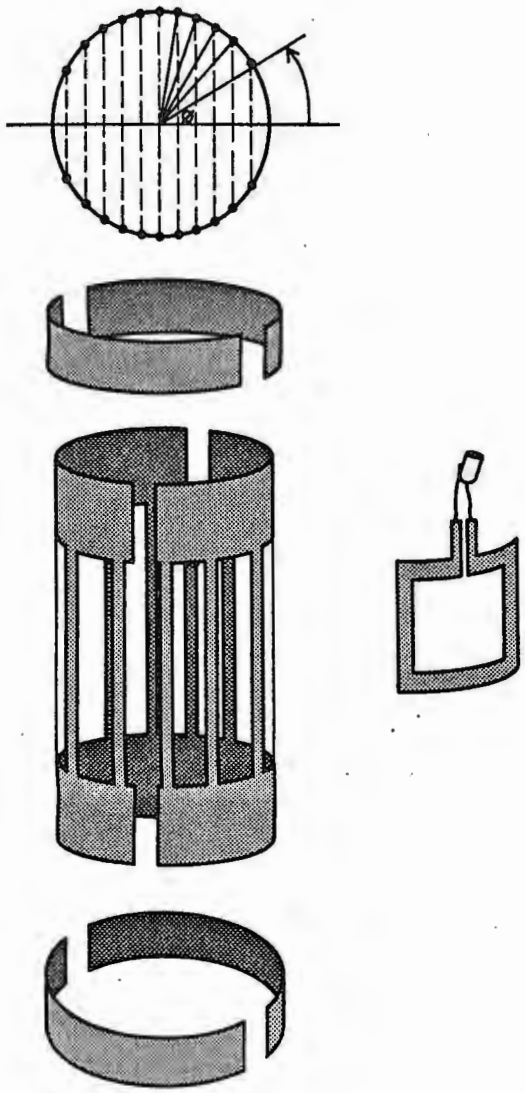
The major features of this coil design are:

1. It is extremely easy and relatively inexpensive to build.
2. It has a very large volume of B1 homogeneity.
3. Contrary to other designs such as a birdcage etc., the whole coil can be treated electrically as a simple inductor and hence one can readily build multiple tuned circuits with this coil.

Thanking you,

Sincerely yours,

Hari Subramanian Lizann Bolinger John S. Leigh



POSTDOCTORAL POSITIONS AVAILABLE

Opportunities for Postdoctoral research in biomedical NMR. Instrumentation available includes 500 MHz, 360 MHz and 200 MHz Bruker spectrometers, and 40 cm bore, 2.0 T and 5.0 T in vivo spectrometers. Applicant should be skilled in modern NMR techniques and instrumentation, or highly enthusiastic about learning these techniques. A keen interest in either metabolic studies in vivo (spectroscopy and imaging of brain, heart, liver, muscle), or high resolution spectroscopy of extracts is a plus, since research opportunities exist in these areas.

If interested please send Curriculum Vitae, biblography and 3 letters of reference to: Dr. John S. Leigh, Professor, Biochemistry and Biophysics, University of Pennsylvania, D501 Richards Building, Philadelphia, PA 19104-6089.

A Poor Man's "Ethernet" Link to the DEC VAX from Nicolet 1280 Computers in the NT Series NMR Spectrometers

C. Allen Bush
Department of Chemistry, Illinois Institute of Technology,
Chicago, IL 60616 U.S.A.
Bitnet address: "GLYCOBUSH @ IITVAX"

The inadequacies of the computers attached to the older NMR instruments such as the Nicolet 1280 supplied with the NT series spectrometers become readily apparent when one attempts some of the currently available 2-dimensional experiments such as phased COSY (DQF COSY). Although the electronics can generate pulse sequences for acquisition of suitable data sets, the computer lacks adequate storage for processing of the large matrices needed to avoid cancellation of antiphase cross peaks multiplets. Similarly the software provided with these older spectrometers lacks many desirable features such as the ability to plot negative and positive contour levels or to integrate cross peak intensities in phased NOESY spectra. An unreasonable effort would be required to modify the assembler coded software to incorporate these features and it would not be possible to explore methods of linear algebra or MEM for extraction of the spectral information from the FID. It has been suggested that these new methods could be very useful in improving the resolution in the f_1 dimension of 2-d NMR by avoiding the severe apodization which accompanies zero-filling necessary in the t_1 dimension.

The obvious solution to the shortcomings of an obsolete computer is to transfer the 2-d NMR data from the instrument computer to a modern general purpose computer for data processing thus freeing the spectrometer to do what it does best, namely to acquire NMR data. As a byproduct of this measure, one gains a simple and efficient method for back-up of data on the tape drive of the general purpose computer as well as faster processing of the 2-d data without the purchase of an array processor for the proprietary instrument computer. Among the several available software packages for processing NMR data on general purpose computers, we have selected the FTNMR package of Dennis Hare. It is especially well suited for analysis of the 2-d NMR data used in our research on the structure and conformation of carbohydrates which exploits technology similar to that used in the biophysical chemistry of proteins and nucleic acids. A major obstacle to the use of a general purpose computer for 2-d NMR data processing is the need for transmitting large data sets. Typically, the raw data in a 256 x 2k x 2 complex data set with phase encoding may involve as much as 6 megabytes of data. Although it is expensive, the ethernet interface offered on the most recent instruments is suitable, but older computers

generally lack this capability and their serial data transfer rates are slow. For older NMR computers with limited disk storage, high speed data transfer on a parallel data port is desirable.

The Nicolet 1280 computer supplied with the NT series spectrometers has a parallel 8-bit port intended for use with a Centronics printer which is capable of high speed data transfers. Support is supplied with the original software for data output on this port. In our laboratory we have connected the output from this port to a serializer intended for remote use of a Centronics printer. Ordinary twisted pair wires lead to the VAX computer site where the data are converted back to parallel form by a second converter. The two converters necessary were purchased from Black Box Corp. of Pittsburgh, Pa. for a total cost of about $600. The parallel output of the Black Box was connected to the VAX Unibus through a DR-11-W interface. The equivalent Q-bus interface is the DRV-11-B which would be suitable for a MicroVax installation. The VAX running VMS provides software support via QIO calls for DMA transfer of data in large blocks to reduce software overhead to negligible levels. Thus the data transfer rate is limited only by the speed of the Black Box serializer which we have chosen for this implementation. If the VAX were in the same room as the NMR spectrometer, one might be able to eliminate the Black Box and do the transfers directly over parallel ribbon cable. The data blocks are transferred from the Nicolet memory directly in native format and written to the VAX disk by a VAX FORTRAN program. A second formatting program is required to convert the native Nicolet character codes and floating point numbers in the data header into standard formats and to convert the NMR data from Nicolet format (20 or 40 bit integers) into 32 bit floating point suitable for processing by the Dennis Hare software.

In our hands the scheme described above is capable of transferring a typical 2-d data set from the CDC Hawk disks on the Nicolet to the VAX in about 10 to 15 minutes. Although a serializer superior to the Black Box would result in improved transfer times, the data transfer is much shorter than the time for acquisition of a typical 2-d data set (4 to 24 hrs.). It will be recognized that since the Centronics port on the 1280 is for output only, handshaking is provided in this scheme only at the byte level. We had anticipated that it might be necessary to use the serial port on the 1280 to receive parity check information on entire data blocks to ensure integrity of the data and to request retransmission of any faulty data blocks. We have not implemented the block parity checking since data errors have not been a problem in more than a year of routine use of this system in our laboratory.

I would like to acknowledge Tom Lew of Toronto for originally suggesting the use of the Centronics port for data output and for substantial help with the software.

355-50

HMRI

HUNTINGTON MEDICAL RESEARCH INSTITUTES

Professor B.L. Shapiro,
TAMU NMR Newsletter,
966 Elsinore Court,
Palo Alto, CA 94303

March 11th 1988
(received 3/17/88)

File transfers from Nicolet 1280 to IBM PC

Dear Professor Shapiro,

Readers of the TAMU NMR newsletter who have Nicolet 1280 computers may be interested in a program we have developed to transfer files to an IBM PC (or equivalent) microcomputer. There were several reasons for the development of the program, the most important one being the need for off-line data analysis. We also wished to be able to transfer data to a more "friendly" programming environment, one which is readily available to a large number of our users. Indeed, with the advent of portable computers (and personal computers at home), our spectroscopists may now also examine their spectra at home, if they so desire!

We have primarily been using this program to download image files (".DAT") recorded on General Electric "CSI" spectrometer; however, it should be equally applicable to other types of data files (and possibly other Nicolet computers if they use the "SECS" file transfer protocol). Use is made of the Nicolet utility program "FILTRN" to transmit data via serial RS-232 port at rates of up to 9600 baud. 19.2 kbaud should be possible over very short distances, although we haven't tried this. The receiving program on the PC converts the Nicolet 20-bit word into a 3 byte/sample format before storing it on disk; if the dynamic range of the data permits (virtually always the case for image files from our system which has a 12-bit ADC) a separate routine can be used to pack this into a 2 byte integer format. This program also discards the file header plus some other garbage. Finally, a routine is available to graphically inspect the downloaded file in either format.

Anybody who is interested in obtaining a copy of these programs (and the source code if desired, written in "Turbo Pascal") should send a blank 5 1/4" floppy disk to me at the address below,

yours sincerely,

Peter Barker

Peter B. Barker

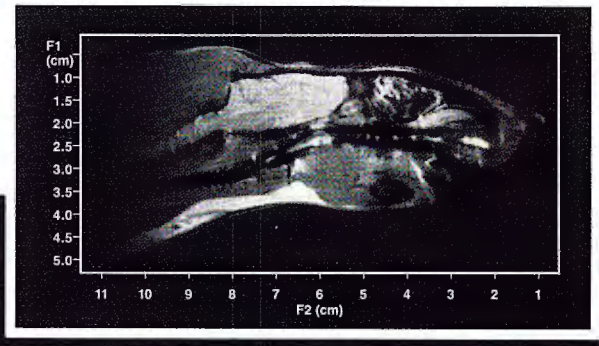
Advanced Neurosurgery Laboratory
Research CT, MR Imaging and MR Spectroscopy Center
10 Pico Street, Pasadena, CA 91105-3201

Now... Whole-body animal imaging spectroscopy at 300 MHz!

A Siemens and Varian joint venture. You benefit from single-source access to systems combining Siemens expertise in clinical MR imaging with Varian's leadership in high-resolution NMR.

Only *Spectroscopy Imaging Systems* gives you both the resources of a large corporation and the innovative responsiveness of a dedicated company. You also receive the combined expertise of site planners, system engineers, technical support personnel, and application scientists.

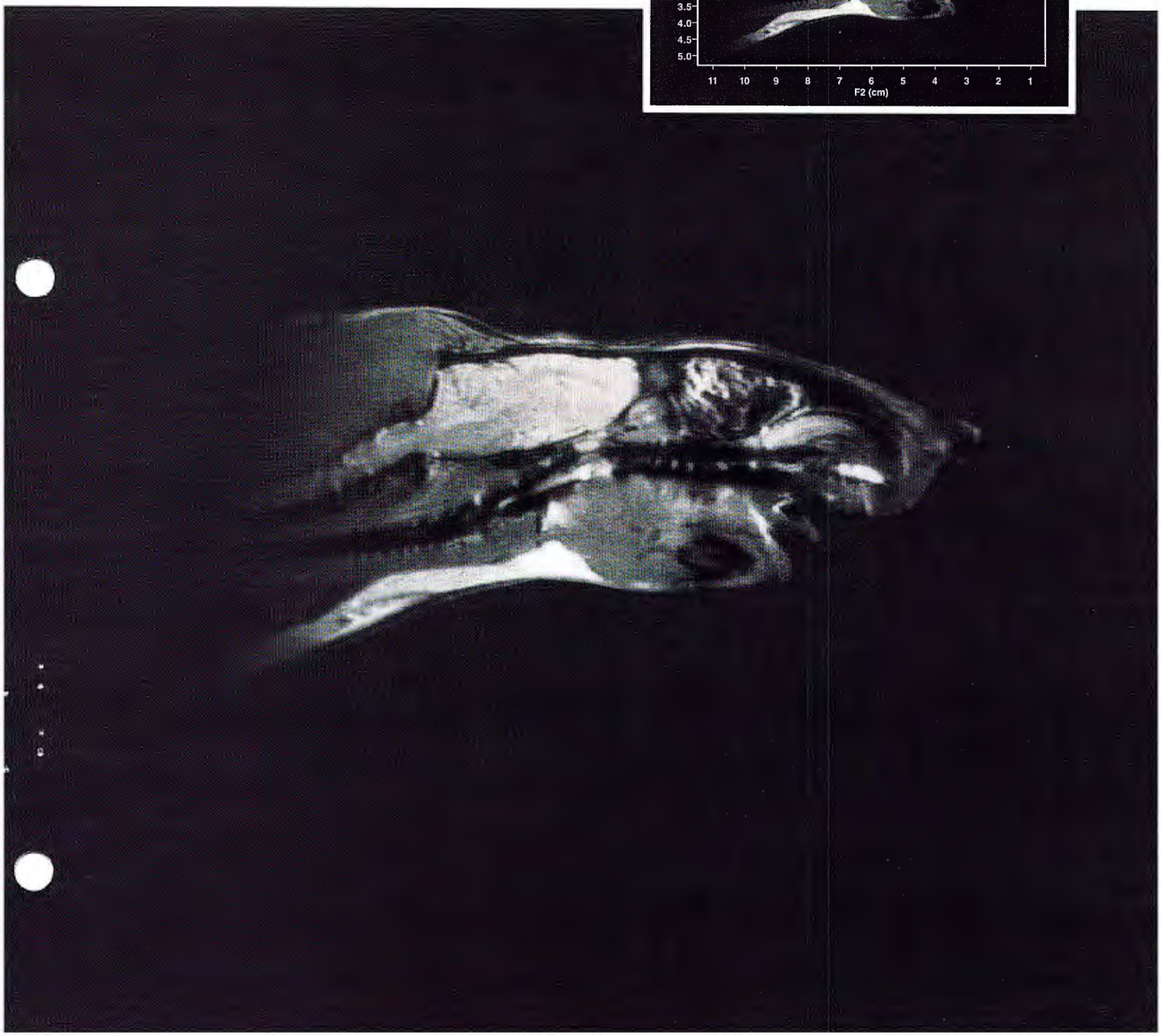
For systems, service and support in imaging spectroscopy, call 415-659-2600 today. Or write to 1120 Auburn Street, Fremont, California 94538.



Spectroscopy Imaging Systems Corporation

A Joint Venture of Varian and Siemens

(415) 659-2600



SIS—A system configuration to fit every need

Imaging spectroscopy is steadily increasing its field of application in a variety of scientific studies. To accommodate the diverse interests of SIS users, a wide range of system configurations allows you to match your instrumentation precisely to your experimental requirements.

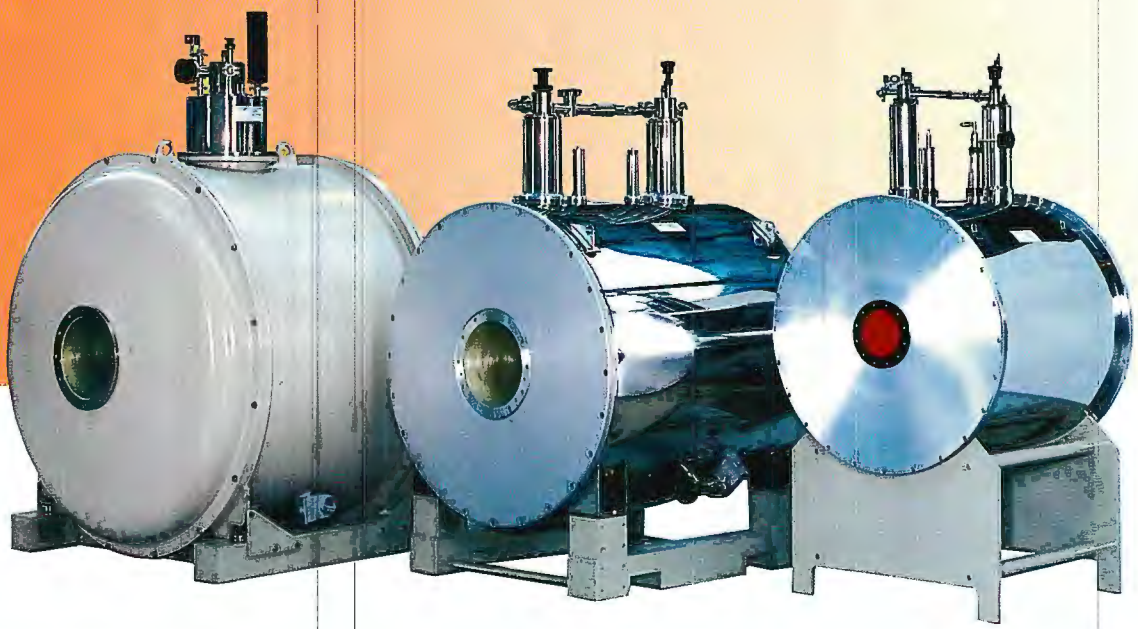
If your experimental needs require configurations beyond the illustrated combinations, our technical staff will help establish the appropriate equipment configuration.

System Configurations

- Single-channel or dual-channel RF
- Broadband to 200 MHz or 300 MHz
- Standard or compact host computer
- 300/180, 200/330, 200/400, or 85/310 magnet systems
- Range of computer peripherals and enhancements
- Additional data station(s) with Ethernet

Magnet	Center Field	Magnet Bore	Clear Bore	Maximum Gradient	Plotted Homogeneity	HHLW Resolution	5 Gauss On-Axis	5 Gauss On-Radius
300/180	7.05T	183 mm	125 mm	4.0 G/cm	80 mm DSV ±6 ppm	35 mm DSV 0.1 ppm	5.60 m	4.45 m
200/330	4.7T	330 mm	254 mm	2.3 G/cm	140 mm DSV ±5 ppm	70 mm DSV 0.1 ppm	6.95 m	5.60 m
200/400	4.7T	400 mm	324 mm	1.8 G/cm	140 mm DSV ±4 ppm	80 mm DSV 0.1 ppm	8.50 m	6.75 m
85/310	2.0T	310 mm	225 mm	3.0 G/cm	100 mm DSV ±5 ppm	70 mm DSV 0.1 ppm	4.50 m	3.63 m

DSV = Diameter Spherical Volume
HHLW = Half-Height Line Width
PPM = Parts Per Million



200/400, 200/330, and 300/180 magnets for the NMR Imaging Spectrometer System.
(Photos courtesy Oxford Instruments.)

Spectroscopy Imaging Systems
1120 Auburn Road
Fremont, California 94538
(415) 659-2600

Note: Equipment described is intended for investigational purposes, and is not approved by the FDA for clinical use.

Carleton University
Ottawa, Canada K1S 5B6

March 10, 1988.
(received 3/16/88)

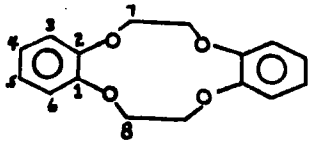
Dr. B.L. Shapiro
966 Elsinore Court
Palo Alto CA
94303 U.S.A.

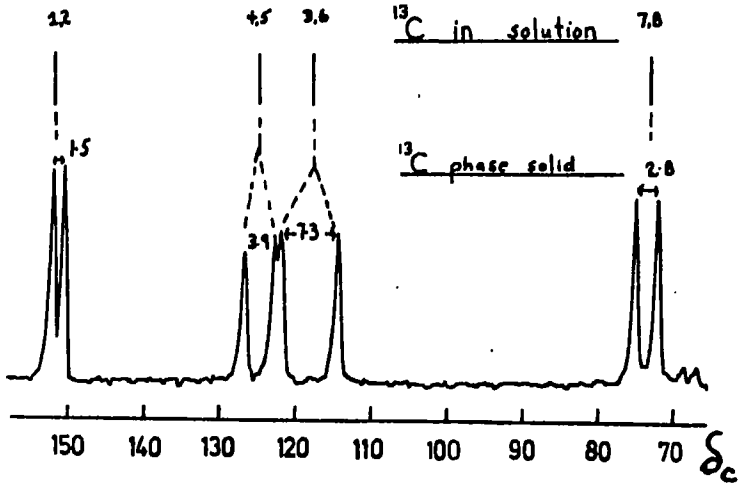
Title: "Solid Phase ^{13}C NMR of Dibenzo-12-Crown-4"

Recently we have become interested in the applications of ^{13}C CPMAS to stereochemical problems in crown ether chemistry. As an example of spectral obtained I enclose that for DB-12-C-4. In solution at room temperature one observes the expected 4 resonances. The solid phase spectrum is much more interesting, with a doubling of resonances due to a stereochemically rigid macrocyclic conformation in the crystal. We have found that the crystal possesses a true molecular centre of symmetry, so that indeed 8 resonances are expected.

The observed chemical shift difference of 7.3 ppm at the ortho-aromatic carbons is worthy of note. The x-ray structure shows a torsional angle of 24.64° for the C3-C2-O-C7 network, while the value for the C6-C1-O-C8 network is 61.64°. We attribute the more shielded resonance to C3, where the steric γ-effect is presumably more pronounced than for C6.

At present we are in the process of calculating (INDO MO) the angular dependence of ^{13}C shifts for O-C-C-O and C-O-C-C torsional networks. Such data have only been calculated previously for the C-C-C-C case in butane.





Sincerely,

G.W. Buchanan, Professor of Chemistry.

Department of Chemistry □ Steacie Building □ (613) 564-2760

UNIVERSITY OF CALIFORNIA, LOS ANGELES UCLA

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
405 HILGARD AVENUE
LOS ANGELES, CALIFORNIA 90024-1569

March 11, 1988
(received 3/14/88)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry,

USES OF NMR SAMPLE CHANGERS IN AN ACADEMIC ENVIRONMENT

Since postdoctoral and graduate student labor is cheap, the purchase of equipment for automatic sample changing for NMR spectrometers in academic labs is often regarded as frivolous by granting agencies, administrators, and even end users who are accustomed to running all spectra manually. From a purely economic point of view, it should be pointed out that NMR spectrometer capital costs and operating costs are anything but cheap and thus any method of increasing the productivity of the spectrometer in an environment where the demand for spectrometer time is heavy should be considered. Sample changers don't eat, sleep, or even answer the telephone. From a more academic point of view, high throughput with minimal intervention by busy human beings will allow some experiments to be carried out that would not otherwise be considered possible due to lack of time.

Our departmental NMR facility has made use of automatic sample changers in a variety of ways for almost three years now. The following spectrometers in our laboratory are fitted with sample changers: 1) 500 MHz (Bruker AM500) with 7 different probes and a large variety of accessories to maximize flexibility, 2) 360 MHz (Bruker AM360) with 2 probes and a smaller variety of accessories, and 3) 200 MHz (IBM Instruments/Bruker AF200) with 2 probes and no other accessories. Additionally, a Bruker data station running the same software is linked via optical fiber to these spectrometers. The availability of some type of off-line processing is essential to the operation of this facility using sample changers.

There are three different modes in which the sample changers are used. The first is operation by the NMR laboratory staff to run service samples submitted by the users. The proton probe is used for maximum sensitivity two mornings per week and the 5mm broadband probe is used for one overnight run where both ^{1}H and ^{13}C spectra are obtained, sometimes with extended signal averaging. This mode is used most heavily for the 500 MHz spectrometer where the user must have adequate training to ensure that the hardware is set up properly for observation of the chosen nucleus. Advantages of this mode are 1) users with no training at all can obtain high field spectra every few days and 2) the operator runs the spectrometer in exactly the same mode on a regular basis including standard samples. This latter advantage provides a form of quality control that may be overlooked in academic laboratories where most samples are run by the users.

The second mode is operation with the sample changer by a particular user

in a time slot scheduled in advance. This mode allows for a great deal of flexibility in obtaining routine spectra provided the user is trained in setting up the hardware properly to observe the desired nucleus. In a regularly scheduled time slot every week, one student sets up and runs up to forty ^{11}B samples in about three hours including ^{1}H decoupled and coupled spectra on each sample. Another group runs several ^{15}N samples including extended signal averaging in one overnight run per week. There have been other examples of use of the sample changer for a large number of spectra on other "X-nuclei" that would not have been done manually for lack of operator time. NMR staff personnel rapidly set up the sample changer for a novice user who then ran the samples. A few groups have such a heavy need for ^{1}H spectra that they designate an operator within their group to gather up the samples and run them using the sample changer in a regularly scheduled time.

The third mode is first-come first-served on the 200 MHz spectrometer using a 5mm probe that is switched under computer control between ^{1}H and ^{13}C observation. The hardware is kept constant on this spectrometer to assure easy operation and fast turn-around times for novice users. This mode is in operation a few hours per day Monday through Friday. Other times the spectrometer is available for experienced users, but the hardware must be returned to the state required for novice users.

The 360 MHz spectrometer is just now being installed. Its sample changer has a bar code reader for labels made for each sample. A 5mm probe that can be switched between ^{1}H, ^{13}C, and ^{31}P under computer control will probably be used the most with the sample changer.

The actual use of the sample changers in our laboratory has evolved in the past as the users needs and equipment availablity have changed. It is clear that the availablity of the automatic sample changers has been extremely important to those experiments that are amenable to automation and has aided those that are not by minimizing the amount of spectometer time devoted to routine work.

Sincerely,

Jane Strouse

Jane Strouse
Director, Instrumentation
Facility

UNIVERSITÉ DES SCIENCES ET TECHNIQUES DU LANGUEDOC

GROUPE DE DYNAMIQUE DES PHASES CONDENSEES

Laboratoire Associé au C.N.R.S. Nº 233

Montpellier, le March 4, 1988
(received 3/15/88)

"NMR ^{13}C signal enhancement by cross polarization in graphitic powders dispersed in a polymer matrix"

P.BERNIER and R.DELTOUR

Dear Pr. Shapiro,

The ^{13}C resonance observation in graphitic powder at room and lower temperature is hindered by the weak natural abundance of these nuclei (1.1%), the wide line powder spectrum (4-5 gauss) and the rather long spin lattice relaxation time ($T_1(T)$ between 2 and 90 minutes). As a consequence various methods have been used to investigate these nuclei, including electrons-nuclei spin polarization transfer by Overhauser effect[1], fast passage techniques[2], high resolution pulse methods[3] and the use of lamellae oriented graphite samples[4].

The techniques used for the powder samples are very much time consuming ranging from hours up to weeks of data accumulation[3].

In order to reduce the observation time, we have dispersed high conductivity carbon black powder particles (Ketjenblack EC) in a polyethylene polymer matrix.
The carbon particles, with a high surface-volume ratio (1200 m^2/gr) have an onion skin structure consisting of fine pellicular graphite lamellae forming connected hollow partly spherical bundles[5].

By cross polarization of the ^{13}C nuclei with the protons of the polyethylene at the surface of the carbon black particles and using magic angle spinning, we have obtained an appreciable increase in sensitivity. This is illustrated in fig. 1, showing the ^{13}C carbon black signal at room temperature after 14 hours data signal accumulation (- 10.000 signal sweeps) using a Bruker CXP Fourier Transform pulse spectrometer at 50.3 MHz.

Place Eugène Bataillon 34060 MONTPELLIER CEDEX — Tél. : (67) 41.30.19 — Télex : USTMONT 490944 F

The line shift of 160 ppm (from TMS) for the graphitic ^{13}C is somewhat smaller than the value (180 ppm) reported for bulk graphite by Suganuma et al.[6] and in the measurements on oriented graphite lamellae of Kume[4];

A tentative explanation which will need more experimental support would be to suggest a redistribution of the electronic wave functions near the surface increasing locally $n(E_F)$ and inducing a Knight shift displacement of about 40 ppm as is the case with intercalated graphite[7]. The possibility of the observation of two carbon sites at the surface as may be apparent in the doublet structure is not excluded.

References

(1) A.Abragam, A.Landesman, J.M.Winter, C.R. Acad. Sci, 247, 1852 (1958).

(2) G.P.Carver, Phys. Rev. B2, 2284 (1970).

(3) J.Conard, H.Estrade, P.Langine, H.Fuzellier, G.Furdin, R.Vasse, Physica 99B, 521 (1980).

(4) K.Kume and Y.MANIWA, Synth. Met. 6, 219 (1983).

(5) K.E. Sichel, Carbon black in polymers composites, M.Dekker edit. (1982).

(6) M.Suganuma, V.Mizutani and T.Kondon, Phys. Rev. B22, 5079 (1980).

(7) K.Kume, K.Nomura, Y.Hiroyama, Y.Maniwa, H.Suematsu, S.Tanuma, Synth. Met., 12, 307-312 (1985).

R. DELTOUR
Physique des Solides
Université Libre Bruxelles
1050 BRUXELLES
BELGIUM

P. BERNIER

UNIVERSITE D'AIX - MARSEILLE - FACULTE DE MEDECINE
CENTRE DE RESONANCE MAGNETIQUE BIOLOGIQUE ET MEDICALE

Unité de Recherche 1186 Associée au Centre National de la Recherche Scientifique

(received 3/17/88)

Professeur Patrick J. COZZONE

Prof. B.L. SHAPIRO
TAMU NMR Newsletter
966 Elsinore Court
PALO ALTO CA 94303

Title : PHANTOM FOR LOCALIZED SPECTROSCOPY

Dear Barry,

The CRMBM is actively involved in research on muscular diseases in animals and humans using a Bruker Biospec NMR system equipped with a 4.7T - 30 cm horizontal magnet. Optimizing pulsing conditions with a surface coil and shimming the magnet can be rather lengthy procedures. They cannot be conveniently performed when the patient - often affected with a form of muscular dystrophy - is already uncomfortably installed with a limb in the magnet. We have found it very practical to conduct most of the adjustments prior to real clinical examination using a pork roast as a phantom. Usually, a 2-pound roast is adequate, especially if you have asked your butcher to shape the roast so that it approximates the section of a human limb. For P-31 spectroscopy, pulsing conditions are calibrated on the Pi peak which dominates the phosphorus spectrum recorded on the roast (Figure 1). The peak of water protons and its separation from the lipid resonance are used to adjust the field homogeneity. Fine adjustments are subsequently completed in a few minutes on the patient or animal limbs. Results are pretty satisfactory as shown on the attached spectrum (Figure 2) which was obtained in 2 min. on the leg muscle of a 50-pound pig, using a home-built 3 cm-diameter surface coil (collaborative work with Dr G. MONIN and Dr G. KOZAK-REISS).

Patrick Cozzone

Sylviane Confort-Gouny

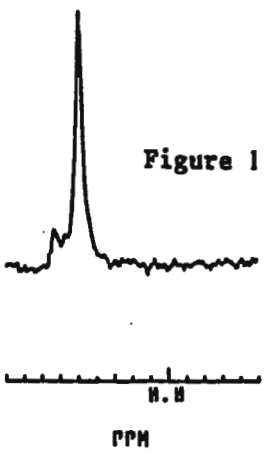


Figure 1

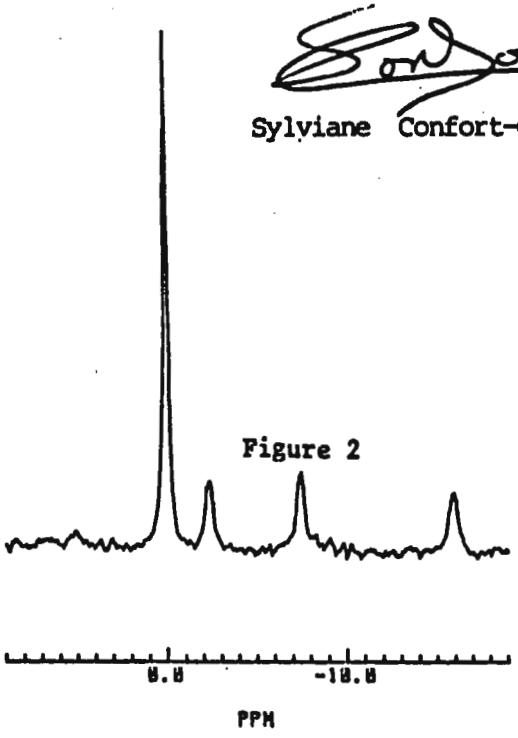


Figure 2

CRMBM - CNRS - Faculté de Médecine - 27 Boulevard Jean Moulin 13005 Marseille - Tél. : 91 79 91 10 poste1506

UNMATCHED VERSATILITY. UNMATCHED POWER.

Whether you're involved in NMR, IR or other spectroscopic techniques, SpecStation computers and networks from New Methods Research offer advanced solutions to your data processing. The high resolution color graphics of SpecStation, combined with our own LAB ONE™ family of sophisticated software, gives you the most powerful laboratory data systems available.

The most advanced NMR data processing available today. All LAB ONE programs—**NMR1, NMR2, MEM/LPM,** and now **IMAGE**—can be run with the optimized SpecStation user interface.

Simultaneous processing of data from *all* brands of NMR instrumentation and several FT-IR instrument types. *All* data is placed in the completely open LAB ONE format.

Compatibility. Choose configurations from both inexpensive desktop graphics workstations and advanced graphics supercomputers like the SpecStation S/3000 (up to 40 times the power of VAX 11/780).

LAB ONE and SpecStation are trademarks of New Methods Research, Inc. VAX is a trademark of Digital Equipment Corporation.

COMPLETE laboratory computer networking with high-speed multi-window graphics at *all* SpecStation nodes. Users can process both locally and remotely so they can effectively share resources—even across *different* brands of computers.

Expandibility. From a single inexpensive NMR data station to an integrated laboratory computer network, SpecStation networks can be configured for large *or* small R&D budgets. So as you grow your system can grow with you.

For a free color product brochure call New Methods Research today.

nmri

New Methods Research, Inc.

719 East Genesee Street
Syracuse, New York 13210
(315) 424-0329 FAX: (315) 424-0356

SpecStation™

LABORATORY DATA STATIONS & NETWORKS

NMRi's Commitment to Excellence

New Methods Research, Inc. is committed to a comprehensive program of customer support and quality assurance services. Several staff members have the specific function of responding to the needs of our current and prospective customers. Customer satisfaction is closely monitored and several channels of communication are available, including regularly scheduled Users' Workshops (locations in Europe, Japan, and several U.S. cities), toll-free phone service, and other software support mechanisms. The NMRi customer support staff provides an interface with programmer-scientists who can respond to your needs.

Continued growth, an expert team of programmers, and professional customer support staff are ingredients for development of the most advanced data analysis software available anywhere. We invite you to call and have us help *you* design a data processing and network environment for your laboratory.

- **Customer support scientists and staff**
- **Comprehensive manuals, status reports, regular software releases**
- **Users' Conferences at NMRi and at local sites**
- **Software report forms to request new features, changes, or report bugs**
- **Toll-free phone service**
- **FAX (315-424-0356) and wide-area network access for rapid communications**

NMRi
New Methods Research, Inc.
719 East Genesee Street
Syracuse, New York 13210
(315) 424-0329 FAX: (315) 424-0356

LAB ONE® INTELLIGENT SOFTWARE FOR THE LABORATORY

DEPARTMENT OF HEALTH & HUMAN SERVICES
Public Health Service

Food and Drug Administration
Bethesda, MD 20205

March 9, 1988
(received 3/10/88)

Dr. Barry Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Frankenstein-ian NMR: An Old World Solution to a New World Problem

Dear Barry;

Finding myself in danger of the pink slip after a stormy return to the TAMU fold, I can only ask for forgiveness and wish you a warm spring season in your new surroundings, and may the single traffic light between you and Pebble Beach be always GREEN.

On a more technical note, I would like to describe our recent solution to what must be becoming a more common problem: Old consoles die, but superconducting magnets live on!! Our old Bruker WM-300 spectrometer, originally purchased in 1980, had reached near expiration in the New World of NMR. It suffered from a small disk drive, no pulse programmer nor decoupler phase shifts to permit sophisticated pulse sequences of 1D, let alone 2D. After many years of fruitful service, we felt drastic measures were in order.

We shopped for a new 300 MHz console among the vendors, and we ended up with a GN-300 system. Our reasons were several and clearly of an individual nature, but I only want to describe how one weds Bruker and GE into a single functional spectrometer.

We retained the magnet, magnet power supply, room temperature shims, variable temperature unit, and probes from the Bruker system. Since both systems operate in a 50 ohm environment, probe interfacing and compatibility was not a problem; however, the major obstacle was to match the lock circuitry of the GN-300 console to the field control system of the Bruker power supply/shim system and to interface the shim gradient controls to the Bruker power supply. The shim gradient interface was accomplished with minimal patch-work via a box adapting voltage levels and connector types. The lock system proved somewhat more difficult!

The response of the GE lock system is much faster than the old Bruker WM-era. This resulted in dramatic oscillations of the lock/field control system–on even the strongest lock signals. Not only was this bad for resolution; it is impossible to shim! The problem was rectified by addition of capacitance to the integrator circuit in the GE lock system (Sorry to reduce performance of a nice circuit, guys!) to match the time response of the field control circuitry of the Bruker power supply. This led to a very happy and operationally transparent system.

The final shot in the magnet has been the addition of new probes from Cryomagnet Systems, Inc. We purchased 5 mm probes for normal broadband operation and a ^{1}H probe equipped with a broadband decoupling coil for indirect detection, etc. The performance of the system (^{1}H S/N 137:1 and ^{13}C ASTM S/N 85:1, both measured in standard thin-wall tubes) is basically the same as a new instrument of a single maker. The performance of the broadband decoupler coil in the ^{1}H probe is especially exciting for $^{1}H\{^{13}C\}$ applications to polysaccharides (*c.f.* Carb. Res., **166**, 47-58(1987) and Tsui, *et al.* Carb. Res., in press).

The broadband decoupler is of my own making. Performance of this unit is not available just yet. Hardware details of the lock circuit modifications are available for anyone who finds themselves in a similar situation. This summer we should be able to provide your readers with some performance reviews of the JEOL GSX-500, since we are expecting replacement of our JEOL GX-400 with a GSX-500 within a month or so.

Best regards,

R. Andrew Byrd
Biophysics Laboratory, FDA
8800 Rockville Pike
Bethesda, MD 20892

P.S. Also, I have an opening for a Postdoctoral position available Fall 1988. The applicant would be involved in solid-state studies of model and biological membranes.

POST-DOC. EARNESTLY SOUGHT:
Time's a-wasting. Come and work on structural investigations by high-field-induced molecular orientation. Ability to synthesize some deuterated compounds helpful. Big pay, stimulating colleagues, lots of 620 Mhz spectrometer time. Telephone or wire A. Bothner-By, Carnegie Mellon University, Pittsburgh, PA, 15213, telephone 412-268-3125.

Spectroscopy Imaging Systems Corporation

A Joint Venture of Varian and Siemens

Spectroscopy Imaging Systems, the Joint Venture of Varian and Siemens has the following positions available.

1. Two Software Engineers. The first position is for development and maintenance of image processing and user-interface software. The second position is for development and maintenance of real-time instrumentation control software.

2. Sales Support Specialist. Responsible for providing direct product technical support to the field sales organization and prospective customers.

3. R.F. Design Engineer. Design of low level signal generation and modulation, low noise preamplifiers, broadband receivers, high power switching and generation.

Interested readers should call Peter Llewellyn (415) 650-2600 or send a resume to the company at 1120 Auburn Street, Fremont, CA 94538.

FOR SALE: Varian EM390 90 MHz NMR with spin decoupler and variable temperature controller, air pump, and manuals. Ten years old; slightly used.

Contact Dr. James Sims, Plant Pathology Department, University of California at Riverside, 92521. Phone: 714-787-4127.

University of Alberta
Edmonton

Department of Biochemistry

Canada T6G 2H7

474 Medical Sciences Building, Telephone (403) 432-3006

Dr. Bernard Shapiro
966 Elsinore Court
Palo Alto, CA 94303
U.S.A.

March 17, 1988
(received 3/21/88)

BACKGROUND RESONANCE IN 5 MM ^{1}H PROBE

Dear Dr. Shapiro,

Thank you for your pink reminder. We would like to report on some interesting background resonance results that we have obtained with our ^{1}H probe. The probe, which is a 5mm ^{1}H photo-CIDNP, will be used on our Nicolet 300 WB spectrometer. When we were building it, two critical questions arose: (a) what epoxy could we use for securing the coil to the insert; and (b) what materials should be used for the internal and optical supports that would produce the minimum background? This prompted us to investigate a selection of compounds. Difference spectra of the compounds, substracting the spectrum of the empty probe, show the varying background resonances that were obtained. The conditions were sw = +/- 50,000 Hz, 32 transients, 5 µsec pulse width, and line broadening 25 Hz.

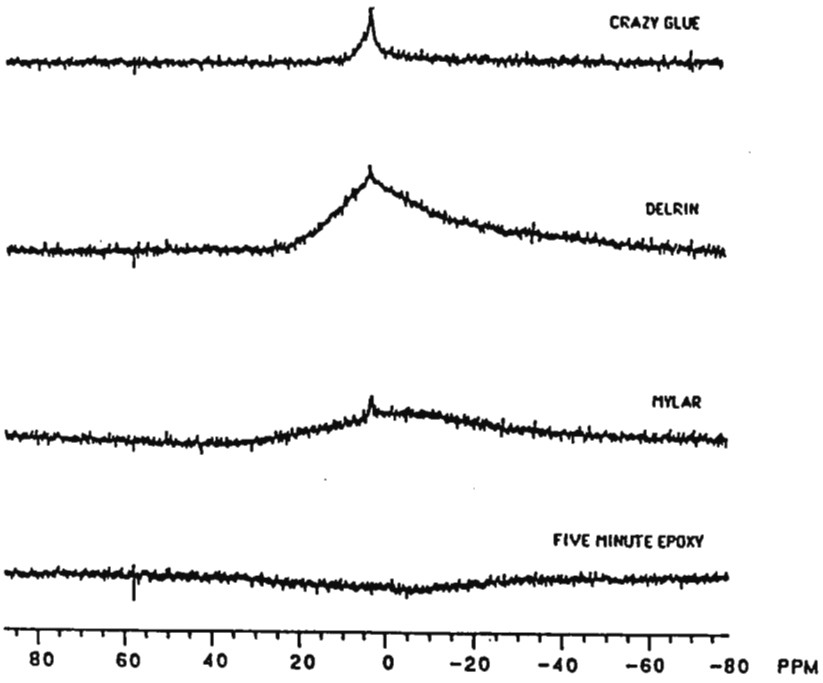
We have since designed a self supporting coil which totally eliminates the use of epoxy.

Please credit this to Brian Sykes' subscription.

Yours sincerely,

Gerry McQuaid.

Gerry McQuaid



355-64

UNIVERSITÄT TÜBINGEN
PHYSIKALISCHES INSTITUT
Prof. Dr. O. Lutz

D-7400 TÜBINGEN 1, den
Morgenstelle
Telefon (0 70 71) 29 67 14

22.02.1988

(received 2/27/88)

Prof. Dr. Bernhard L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303
U.S.A.

Heteronuclear Imaging: ^{23}Na, ^{27}Al, ^{51}V

Dear Barry,

in the last time we try to transform our experience in the field of the usual heteronuclear spectroscopy to tomographic and spectroscopic investigations on a whole body Siemens Magnetom working at 1.5 Tesla. In fig. 1 a spectrum of the nucleus ^{51}V is presented which has been obtained with the standard ^{23}Na head coil of the imager. Some further results on imaging with hetero-nuclei are given in the paper: ^{23}Na, ^{27}Al, and ^{51}V Multinuclear NMR - Imaging and NMR - Spectroscopy with a 1.5 T Imager: M. Braun, O. Lutz, W.I. Jung, C.S. Kischkel, R. Oeschey, M. Pfeffer, Z. Naturforsch. 42a, 1037 (1987).

Another well known spectroscopic technique, the selective non excitation of special spectral lines has also been transformed to the requirements of whole body imagers. With the five pulse SENEX - sequence images of the water or the fat distribution can be obtained with high signal-to-noise ratio and independently of the homogeneity of the RF - field. A paper appeared recently in Z. Naturforsch. 42 a, 1391 (1987): Selective Non - Excitation of Water or Fat Protons in Magnetic Resonance Imaging by M. Braun, W.I. Jung, O. Lutz, R. Oeschey.
Applications are running in cooperation with the colleagues of the Radiologische Universitätsklinik Tübingen.

Sincerely

(Otto Lutz)

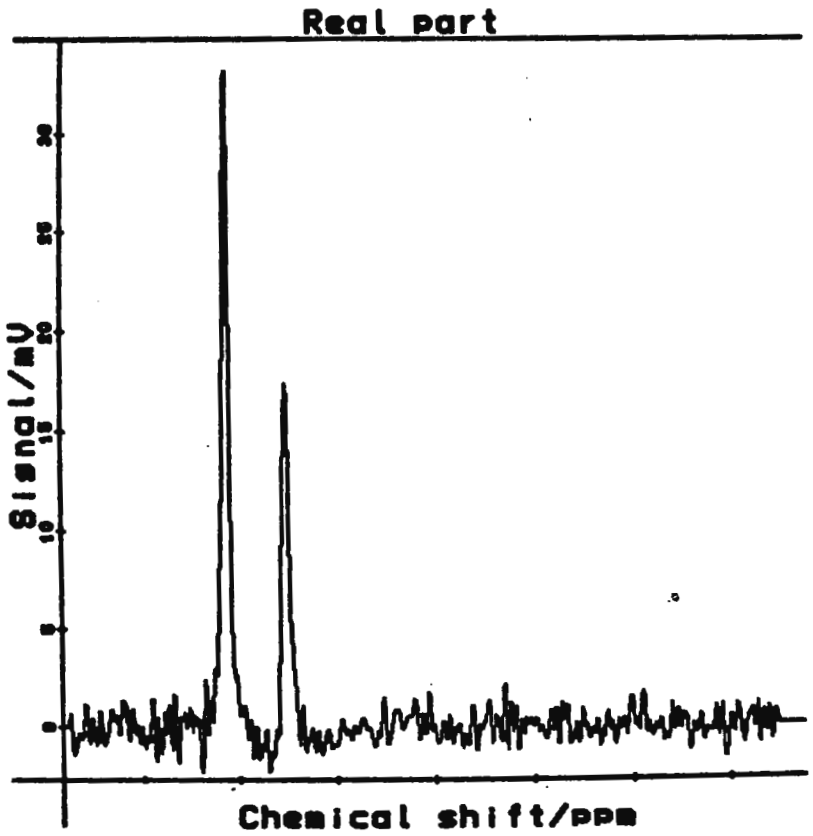


Fig. 1: ^{51}V spectrum of a 0.14 molal alkaline aqueous solution of $NaVO_3$, using the ^{23}Na head coil of the 1.5 T imager. The signal arise from the VO_4^{3-} (large peak) and the $V_2O_7^{4-}$ species; their chemical shift difference amounts to 23,8 ppm. 32 acquisitions.

DOW CORNING

February 23, 1988
(received 3/17/88)

Professor Bernard L. Shapiro
966 Elsinore Court
Palo Alto, CA 94303

SUBJECT: 2-D APPLICATION OF INAPT

Dear Professor Shapiro:

Greetings from Dow Corning.

Assignment of the structure in Figure 1 was straightforward from a C-C autocorrelated double quantum coherence experiment[1] except for the sterochemistry about the ene. It was much too crowded for NOE to be useful so we had to resort to analysis of the long range C-H coupling constants from the vinyl proton to carbons across the double bond.

Bax's INAPT experiment[2] is ideal for transferring polarization from a single resolved proton to carbons 2, 3 or 4 bonds distant. When the Δ_2, delay is incemented, Figure 2, a selective long range heteronuclear ^{2D}J resolved experiment is created, Figure 3. The long range H-C coupling constants now available are very useful for sterochemical assignments. This modification is similar to Nagayama's[3] except that here all the proton pulses are soft. This is necessary on Nicolet NT series spectrometers that only allow rapid switching of the decoupler power between two levels.

Figure 1 shows the aliphatic correlations and coupling constants obtained from the 2-D INAPT experiment with the vinyl proton selected. The large 10Hz coupling to the methylene carbon at 36.9 ppm must be the three bond coupling constant trans to the vinyl proton and thus the stereochemistry of the ene is established.

This experiment should be applicable to the solution of many such stereochemical questions.

Best Regards,

Dick

Norman Rabjohn, Professor
Michael S. Tempest, Assistant Professor
Department of Chemistry
University of Missouri-Columbia

Richard B. Taylor
Project Chemist
Analytical Research
Dow Corning Corporation

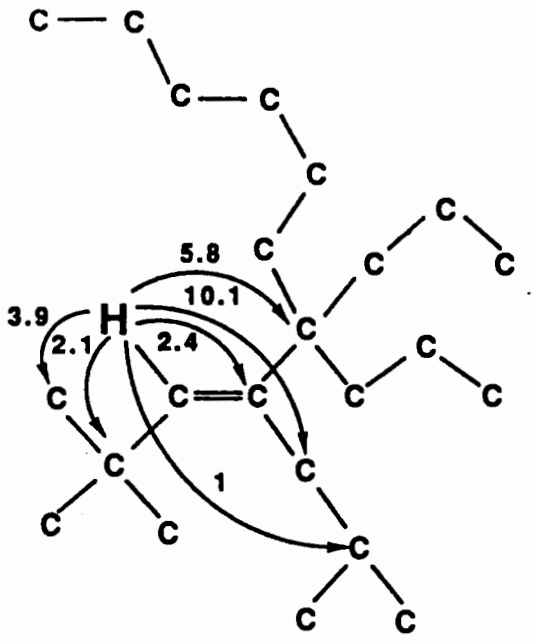


FIGURE 1

A $C_{23}H_{46}$ OLEFIN

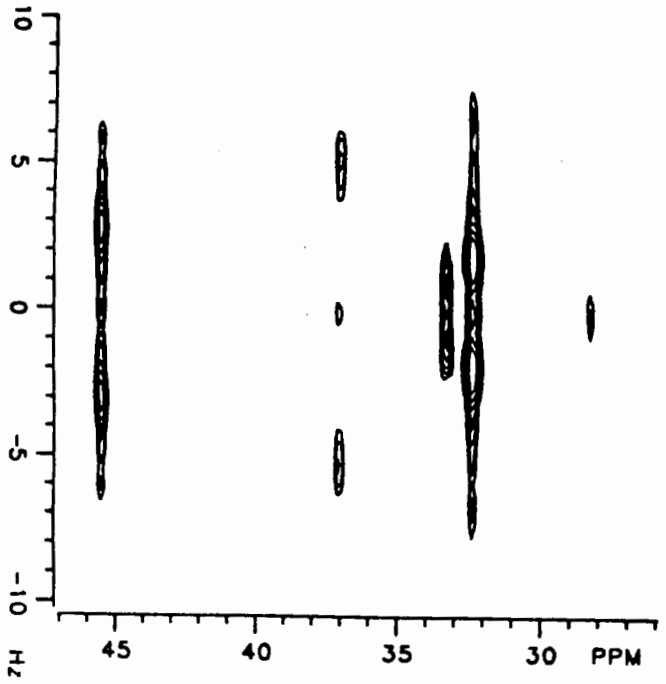


FIGURE 3

ALIPHATIC REGION OF THE 2D-INAPT SPECTRUM

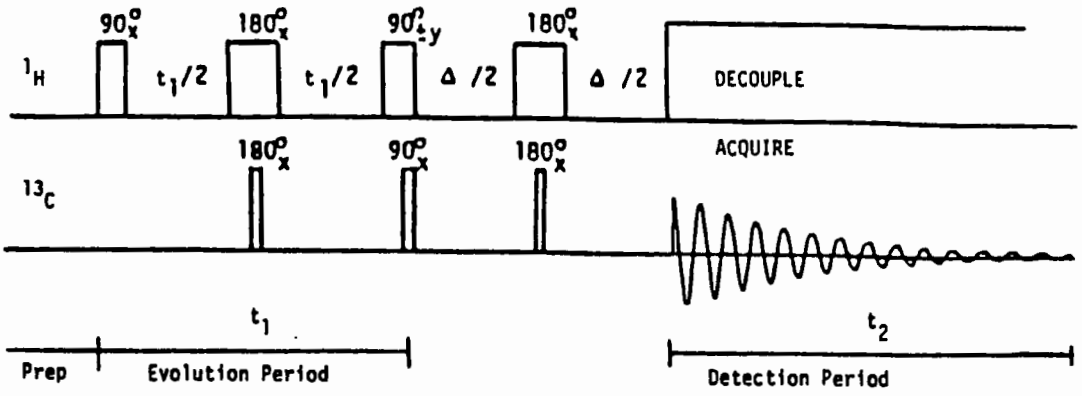


FIGURE 2: Basic pulse sequence of 2-D INAPT. All proton pulses are soft and applied to a single proton resonance. This affords a selective long range heteronuclear 2DJ resolved spectrum, Figure 3.

[1] Turner, D.L. Mol. Phys. 1981, 44, 1051-1058; Turner, D.L. J. Magn. Reson. 1982, 49, 175-178; Turner, D.L. J. Magn. Reson. 1983, 53, 259-271.

[2] Bax, A. J. Magn. Res. 1984, 57, 314-318; Bax, A.; Ferretti, J.A.; Nashed, N.; Jerina, D.M. J. Org. Chem. 1985, 50, 3029-3034; Taylor, R.B.; Corley, D.G.; Tempesta, M.S. J. Nat. Prod. 1986, 49, 670-673.

[3] Jippo, T.; Kamo, O.; Nagayama, K. J. Magn. Reson. 1986, 66, 344-348.

355-68

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service

National Institutes of Health
National Institute of
Environmental Health Sciences
P.O. Box 12233
Research Triangle Park, N.C. 27709

March 8, 1988
(received 3/14/88)

Dr. B.L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Title: Minimization of Baseline Artifacts in Phased 2D NMR

Dear Barry:

As anyone who has had experience with phased, absorption mode 2D-NMR probably knows, baseline curvature in the f_2-dimension can play havoc with the presentation and interpretation of the data set. As described in detail by David Hoult et al. (JMR 51, 110, 1983), a major source of the curvature comes from the transient response of the audio filters to the incoming signal. By adjusting the time after the observe pulse one begins to sample the FID, one can minimize this distortion substantially. For some 2D experiments, however, this not enough.

The problem is that, to a first aproximation, each point in the f_2-domain is modulated by a term proportional to $\Sigma_i M_i^{\circ} \cos 2\pi\delta_i t_1$, where δ_i is the chemical shift of the i-th spin (In phased 2D, a separate data set modulated by $\sin 2\pi\delta_i t$ terms is also generated). After transformation from $t_1 \rightarrow f_1$, this modulation now appears, when viewed in the f_1-dimension, as an image of the entire spectra on each f_2-file. Aside from the fact that these image spectra may show up as ugly ridges parallel to the f_2-axis in a 2D contour plot, they can also obscure the interpretation when spectra with true crosspeaks and false image peaks superimpose.

To illustrate our point, we show in Figure 1A, spectra from the initial files of 2D NOESY experiments on 0.05M Gramicidin S in DMSO-d_6 using a mixing time for cross-relaxation of 0.1 sec. The problem created by the curved baselines can be seen in 1B, which show f_1-slices taken through the Leu $C_\alpha H$ peak at 4.55 ppm. Although the major cross peak with the PheNH at 9.12 ppm is readily observed in all three spectra, the presence of smaller cross peaks signifying weaker or long range dipolar cross relaxation with the LeuNH, (8.36 ppm); $C_\beta H_2$ (1.35 ppm) and $C_\delta H_3$ (0.82 ppm) groups is quite ambiguous in the top and bottem spectra of 1B. The source of the ambiquity can be seen in 1C, which shows slices taken at 4.60 ppm, two files to the left, where there are no lines in the f_2-domain (except for a little bit of the low field wing of the Leu$C_\alpha H$ resonance).

The spectrum with the flat baseline was generated by inserting a delay and a 180° refocusing pulse between the observe pulse and the receiver 'on' flag, so that the FID reaches a maximum sometime after the receiver and the A/D converter have been turned on. Data points sampled before the maximum were discarded by left shifting prior to apodization and Fourier transformation.

A Few Useful Compounds from ISOTEC INC.

A Matheson, USA Company

CAT. NO.	COMPOUND[§]	QUANT.[†]	PRICE[‡] U.S.$
84-70001	Deuterium-depleted Water (<0.5 ppm D)	25g	25.
		4 x 25g	90.
		10 x 25g	200.
		1kg	500.
82-70001	Deuterium Oxide (99.9 atom % D)	100g	45.
		5 x 100g	215.
		10 x 100g	425.
		1kg	400.
82-79041	Deuterium (gas) (99.8 atom % D)	25L	50.*
		50L	75.*
		100L	140.*
		500L	650.*
83-00005	Methanol-^{13}C	1g	105.
		5g	400.
		10g	775.
83-00508	Iodomethane-^{13}C	1g	35.
		5g	165.
		10g	310.
		25g	725.
83-70005	Potassium Cyanide-^{13}C	1g	100.
		5g	415.
		10g	775.
83-70006	Sodium Bicarbonate-^{13}C (>98 atom % ^{13}C)	1g	50.
		5g	200.
		10g	300.
		25g	750.
83-02014	Sodium Formate-^{13}C	1g	120.
		5g	500.
		10g	900.
83-02015	Sodium Acetate-1-^{13}C	1g	40.
		5g	175.
		10g	340.
		25g	800.
83-02018	Sodium Acetate-2-^{13}C	1g	85.
		5g	375.
		10g	725.
83-02020	Sodium Acetate-1,2-$^{13}C_2$	1g	175.
		5g	825.

CAT. NO.	COMPOUND[§]	QUANT.[†]	PRICE[‡] U.S.$
83-84003	Toluene-α-^{13}C	0.5g	210.
		1g	360.
83-84002	1,2-Dimethyl-$^{13}C_2$-benzene (*o*-Xylene)	0.25g	160.
		0.5g	275.
		1g	475.
83-84019	1,3-Dimethyl-$^{13}C_2$-benzene (*m*-Xylene)	0.25g	160.
		0.5g	275.
		1g	475.
83-84009	1,4-Dimethyl-$^{13}C_2$-benzene (*p*-Xylene)	0.25g	160.
		0.5g	275.
		1g	475.
83-42001	Octanoic Acid-1-^{13}C	1g	105.
		5g	375.
83-42015	Decanoic Acid-1-^{13}C (*n*-Capric Acid)	1g	100.
		5g	375.
83-42004	Dodecanoic Acid-1-^{13}C (Lauric Acid)	1g	95.
		5g	350.
83-02030	Hexadecanoic Acid-1-^{13}C (Palmitic Acid)	1g	90.
		5g	350.
83-42011	Octadecanoic Acid-1-^{13}C (Stearic Acid)	1g	105.
		5g	375.
83-02030	Hexanedioic Acid-1,6-$^{13}C_2$ (Adipic Acid)	0.5g	245.
		1g	410.
83-12205	L-Alanine-3-^{13}C	0.5g	200.
		1g	355.
83-12301	L-Aspartic-3-^{13}C Acid	0.05g	200.
		0.1g	375.
		0.25g	750.
83-12302	L-Aspartic Acid-4-^{13}C	0.1g	150.
		0.25g	300.
		0.5g	475.
83-12308	L-4-Hydroxyphenylalanine-3-^{13}C (Tyrosine)	0.1g	400.
		0.25g	900.
83-12202	L-Phenylalanine-3-^{13}C	0.1g	175.
		0.25g	285.

[§]All ^{13}C-labelled compounds are a minimum 99 atom % ^{13}C unless otherwise stated.
[†]Please request prices for quantities that you do not see listed.
[‡]Prices are FOB Miamisburg, Ohio for delivery in North America; please request prices for delivery to the other continents.
*Cylinder charge, please request prices.

3858 Benner Road • Miamisburg, Ohio 45342 U.S.A.
(513) 859-1808 • (800) 448-9760 • Telex: 288278 • Fax: (513) 859-4878

About Isotec Inc.

Isotec Inc. has been separating and enriching the noble gas stable isotopes, including ^{3}He, ^{21}Ne, ^{83}Kr, ^{129}Xe and ^{131}Xe, for approximately eight years. About five years ago, *Isotec Inc.* began the separation and enrichment of the stable isotopes of carbon, nitrogen and oxygen. Now we're making compounds (a few of which are listed on the other side of this page) from these raw materials (and deuterium).

Please let us know what you need—isotope, compound, quantity—we may already have it in stock; if not, we will be pleased to quote on your needs. Remember that there are significant cost advantages to producing one's own stable isotope enriched raw materials. Let us help you take advantage of our advantages.

We would also be interested in your requirements for enriched ^{17}O—desired enrichment, acceptable enrichment, preferred form and quantity. It's somewhere in our columns; we hope to be able to provide you with enriched ^{17}O within the year—your input now will help us do this more efficiently and economically.

If you haven't received a copy of our Interim Price List, which looks something like the figure to the right, please ask us to send you one.

It lists hundreds more products (including all the noble gas stable isotopes, ^{15}N-and ^{18}O-labelled compounds, ^{12}C-, ^{14}N- and ^{16}O-labelled compounds and a large selection of metal isotopes, many of which have a nuclear spin) than are listed on the other side of this page—and more package sizes for many of those listed on the other side.

INTERIM PRICE LIST
3/88

STABLE ISOTOPES

FOR

RESEARCH AND INDUSTRY

ISOTEC INC.

A Matheson®, USA Company

3858 BENNER ROAD
MIAMISBURG, OH 45342
(513) 859-1808 (800) 448-9760
TELEX: 288278
FAX: (513) 859-4878
EASYLINK: 62014510

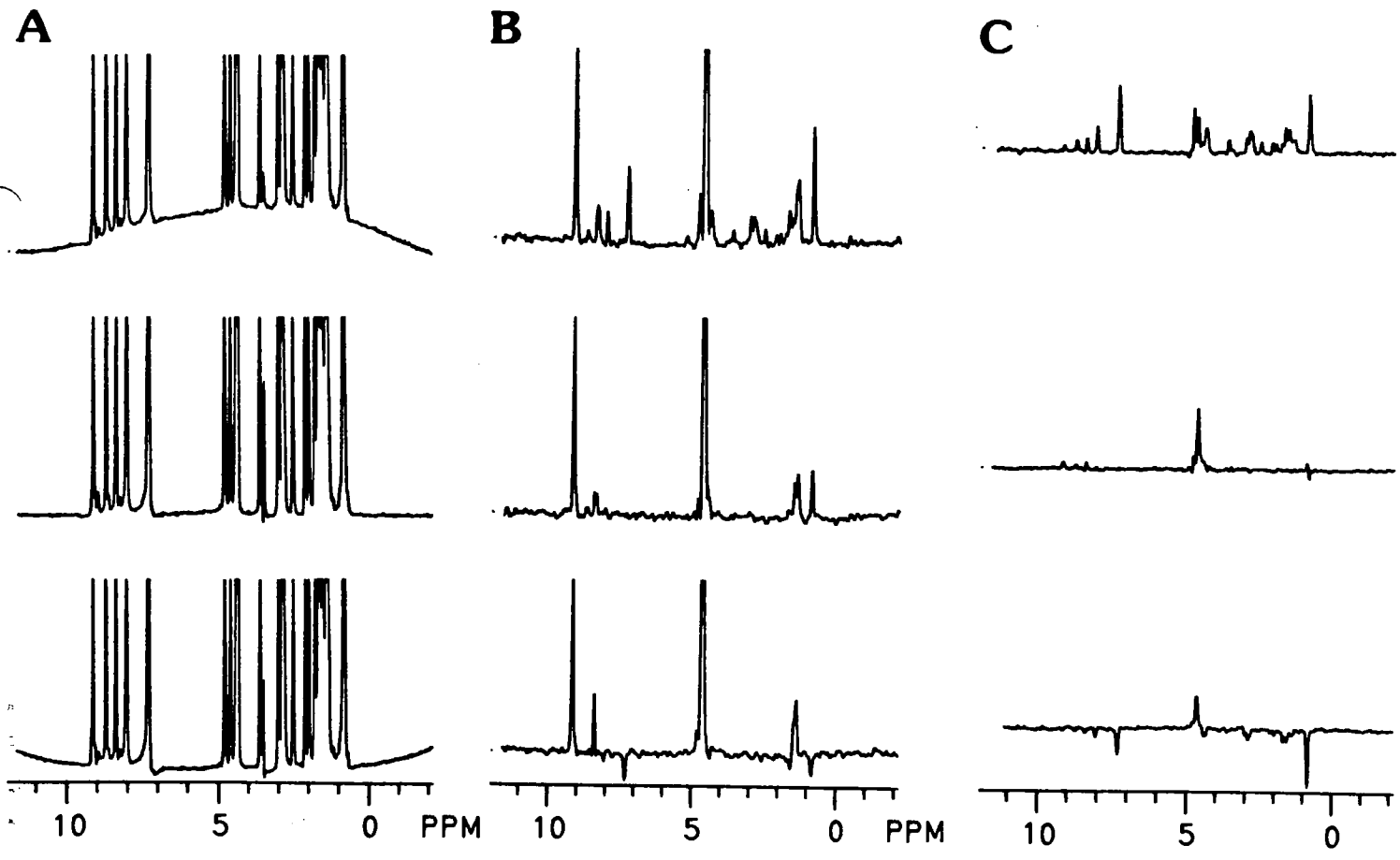
All spectra were accumulated using a 200 μsec homospoil pulse during the mixing period and a 16-step phase cycling scheme per t_1 interval (256 intervals in all). In the experiment with the extra refocusing pulse, the 16 steps included an EXORCYCLE rotation of the phases of that pulse and the receiver.

This contribution is to be credited to Barry Selinsky's subscription.

Best regards,

Don

Dr. Donald G. Davis
Laboratory of Molecular Biophysics



355-72

UNIVERSITY OF CALIFORNIA, RIVERSIDE

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY

RIVERSIDE, CALIFORNIA 92521-0403

March 15, 1988

Professor Barry Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Title: One Dimensional and Two Dimensional Multiple Quantum Filtered ^1H NMR of Monomeric Insulin

Dear Barry:

The recently successful installation of a GN-500 spectrometer in our laboratory finally enabled us to apply some of the more sophisticated NMR experiments to our research.

As our title suggests, we want to report some triple quantum filtered 1D and 2D data on monomeric insulin (M.W. ~7000) and show how they simplify the aromatic region and help us in the assignments of tyrosine, phenylalanine and histidine residues.

Figure 1A-B compares the one pulse ^1H spectrum of insulin to the 3QF 1D spectrum of insulin using a pulse sequence as follows:

$$90°-\Delta_1-180°-\Delta_1-90°-\Delta_2-90°-Acq.$$

Since spins in tyrosine and histidine residues normally do not possess triple quantum transitions, they are effectively edited out in the 3QF 1D spectrum.

Figure 2A and B show the contour plots of COSY and 3 QF-COSY experiments of the aromatic region of monomeric insulin. In the 3 QF-COSY only spins from phenylalanine residues are present and their connectivities are established by the cross peaks.

The pulse sequence is as follows:

$$90°-t_1-\Delta_1-180°-\Delta_1-90°-\Delta_2-90°-Acq(t)$$

where Δ_1 in both sequences is approximately $\frac{1}{4J_{HH}}$ (i.e. 30 MS) and Δ_2 is 5-10 μs.

We shall discuss the complete assignments of the aromatic region and the pulse sequence including the phase cycling scheme in our forthcoming publication. This work was carried out in collaboration with the Novo Research Institute (Bagsvaerd, Denmark), and the monomeric insulin sample was provided by Novo. Please credit this to Dr. Robert W.-K. Lee's subscription.

Sincerely,

Robert W Lee
Robert W.-K. Lee
Academic Coordinator

Michael F. Dunn
Professor of Biochemistry

Melinda Roy
M. Roy

RWK:nc

Enclosure

Figure 1

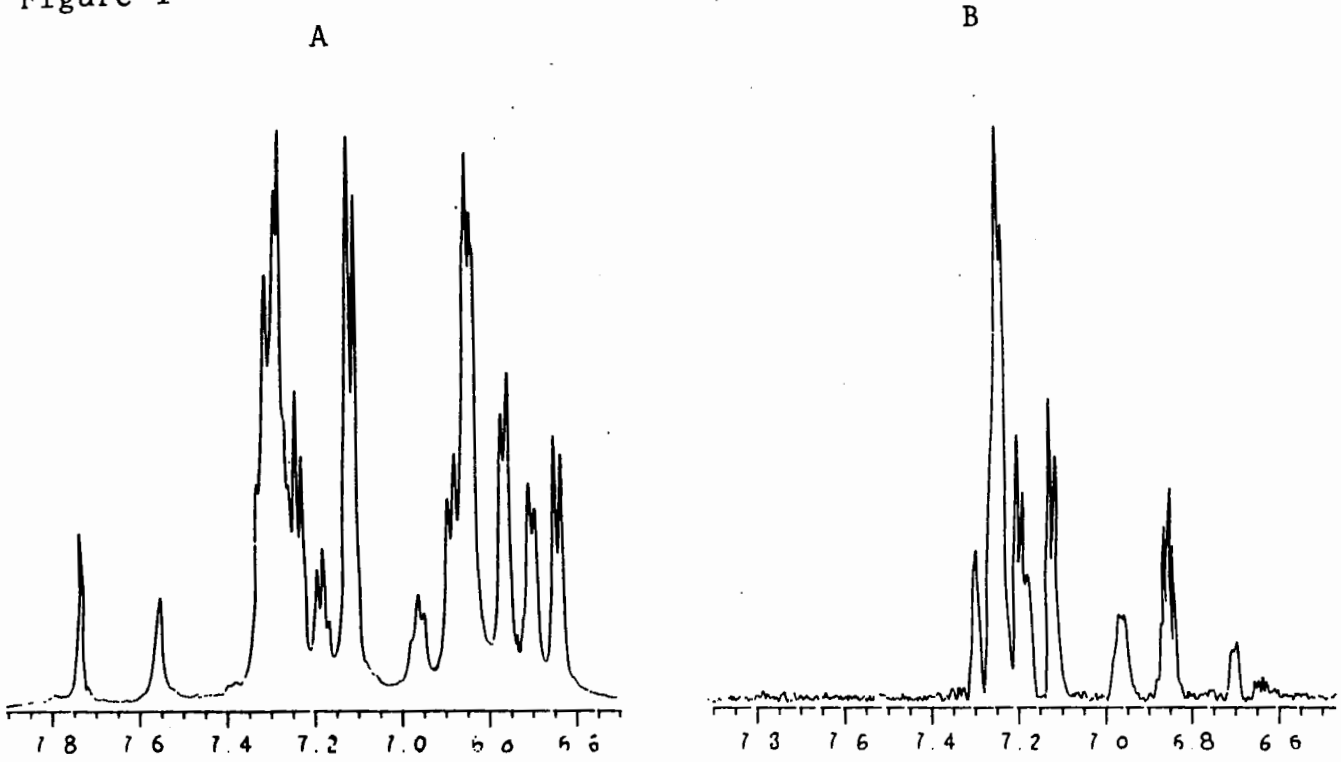
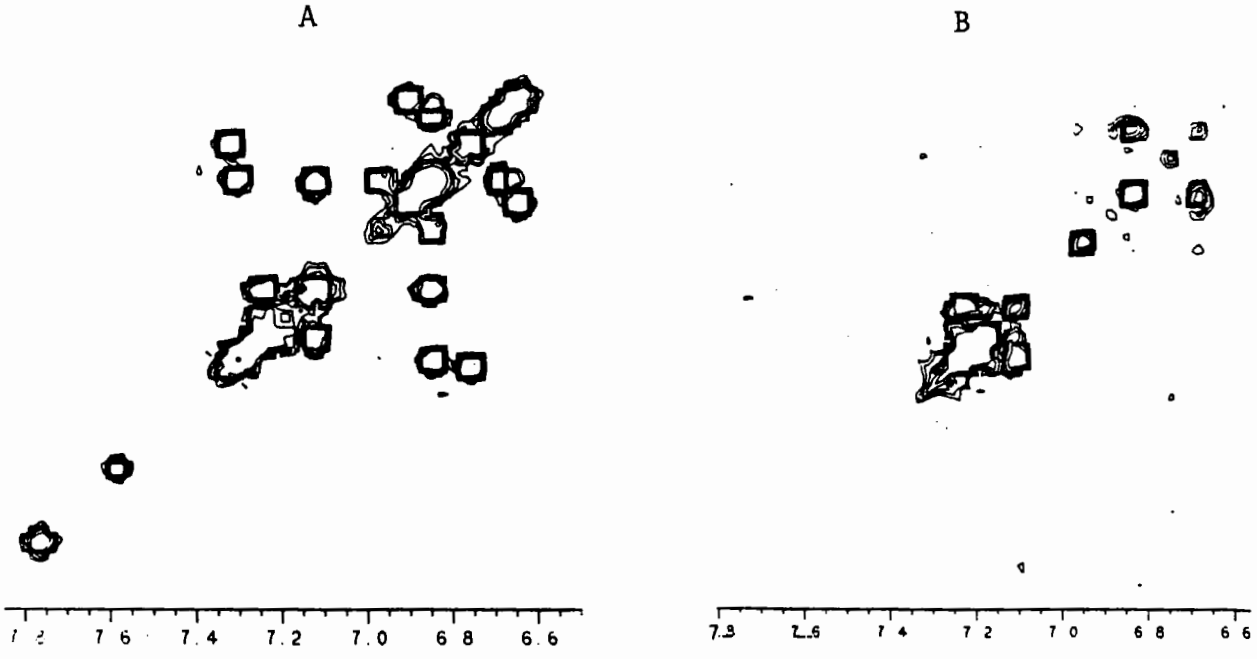


Figure 2



355-74

SOCIETE ANONYME DE DIFFUSION DE L'INSTRUMENTATION SCIENTIFIQUE
BRUKER SPECTROSPIN

Départements :
Spectrométries de Résonance Magnétique
Spectrométrie Infra-rouge Fourier
Imagerie par Résonance Magnétique (IRM)
Spectroscopie de Résonance Magnétique "in vivo"
Aimants & alimentations stabilisées
Mesures de Susceptibilité magnétique
Recherche Océanographique

Siège social :
67160 WISSEMBOURG (France)
34, rue de l'Industrie
Boîte Postale N
Tél. 88.94.98.77 + - Télex BRUSPIN 870 639
Télécopieur 88 54 29 08

Agence Région Parisienne
91320 WISSOUS
Z.I. de Villemilan - 17, Boulevard Arago
Tél. 69.30.71.70 - Télex BRUSPIN 692 644

SADIS BRUKER SPECTROSPIN, Boîte Postale N 67160 WISSEMBOURG

Dr. Bernard L. SHAPIRO
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
PALO ALTO, California 94303

U.S.A.

N./Réf. 88 03 129 CB/AF
V./Réf.

Wissembourg, le 16th of March, 1988

TRANSITION METAL INDIRECT DETECTION

Dear Barry,

Although the very first indirect detection experiments were accomplished on "non common" nuclei (N14, Hg199, ...), everybody is now applying these sequences on C13 or N15 isotopes.

I think that inorganic/organometallic chemists should use this detection scheme more often as it allows very comfortable experimental conditions (5 mm tubes, no enrichment, 10^{-2} M solutions), for very unsensitive but important nuclei (Fe 57, Os187, Rh103, ...).

Of course, indirect detection of these transition metal MR requires a slightly different approach when compared to C13 or N15 work, because :

- the H1 (F19, P31) X coupling may be unknown,
- the X chemical shift range can be spread over 20.000 ppm.

For this purpose, we developped a microprogramme, based on a 2Q heteronuclear sequence, which automatically steps through a wide X frequency range, recording the H1 (F19, P31) response of the X satellites for an array of JH1-X coupling constant values.

The attached figure examplifies such an automated procedure, run on an AM 400.

The knowledge of those two parameters (J value and δ Fe range) makes very easy the start of the 2D version of the double quantum experiment to precisely measure the X chemical shift.

Best regards,

Christian
C. BREVARD

Compound with courtesy of Prof. R. BENN (Uni. Mulheim)

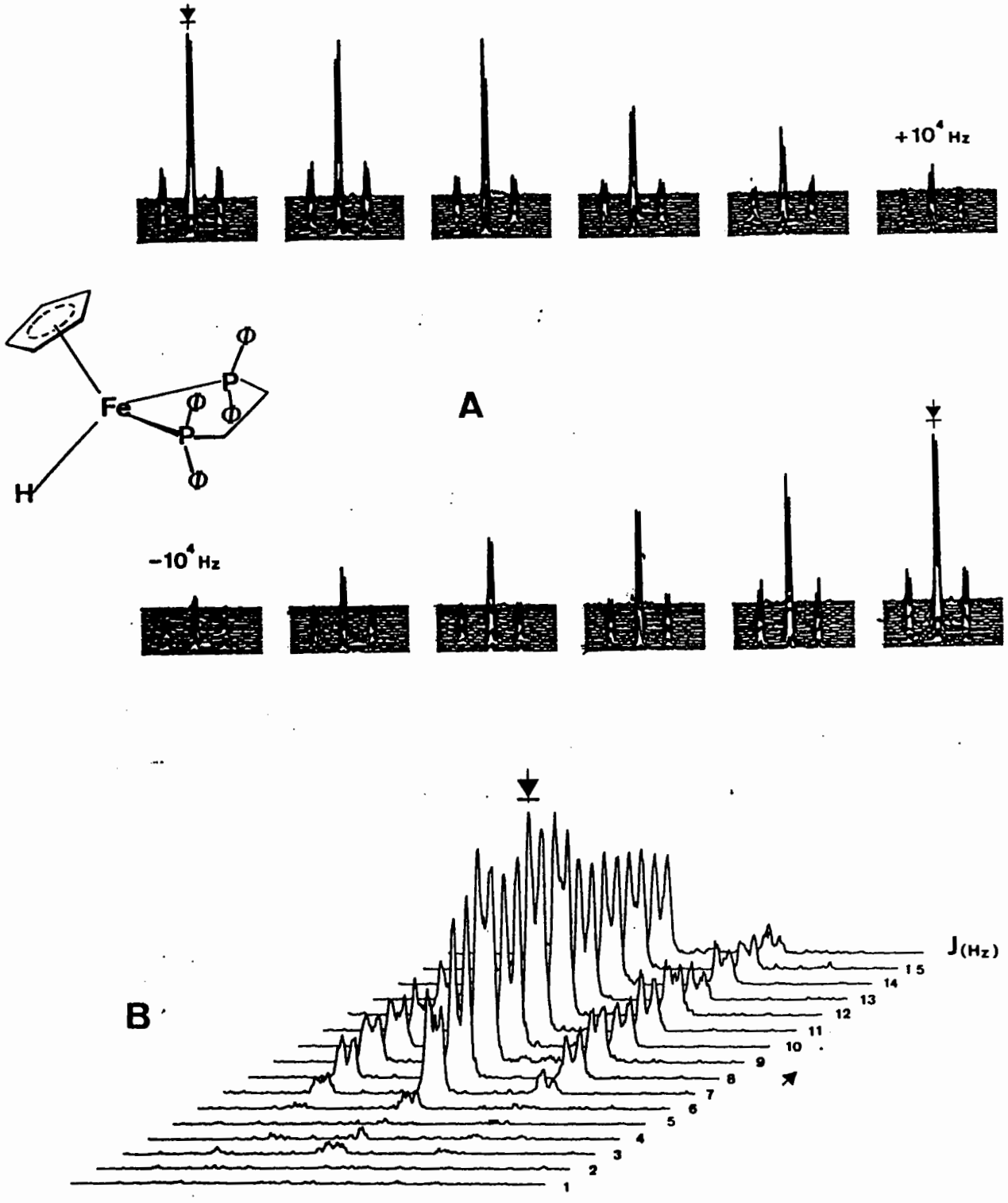


Figure A : Frequency/Coupling search (X = Fe). Note the clearcut/maximum (arrow) at one precise frequency value in the Fe57 frequency space. Note also the explored Fe57 chemical shift range : 1540 ppm.

Figure B : is an expansion of the arrowed region which again shows clearly a maximum response around the 1JH1-Fe57 value (9 Hz).

355-76

國 立 清 華 大 學
NATIONAL TSING HUA UNIVERSITY
HSINCHU, TAIWAN 300
REPUBLIC OF CHINA

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

March 17, 1988

Professor Bernard L. Shapiro
966 Elsinore Court
Palo Alto, CA 94303
U. S. A.

"2QF-COSY Spectrum of Cobrotoxin in Aromatic reagion"

Dear Professor Shapiro:

Cobrotoxin, contains 62 amino acid residues (Mr6949) with four disulfide bridges, is a neurotoxic protein isolated from the venom of Taiwan cobra (Naja naja atra). This protein blocks the neuromuscular transmission at the post-synaptic membrane by the specific binding to acetylcholine receptors.

Shown in the Figure is a 2QF-COSY spectrum of aromatic region for a 20 mM cobrotoxin in D_2O (pH=3.6). There are two tyrosines, two histidines, and one tryptophan residues that cause resonances in the plot. From the coupling pattern in 2QF-COSY spectrum, we can assign tryptophan and tyrosines resonances unambiguously and they are labelled on the top of convensional 1D spectrum. As to those two isolated siglets, labelled with "*", are due to C4 protons of His-32(δ=7.36) and His-4(δ=7.05).

The 2QF-COSY experiment were recorded on our Bruker AM-400 spectrometer equipped with an Aspect-3000 computer. A shifted sine bell window function was applied on both dimensions, and spectrum were not symmetrized.

Sincerely,

Chi-Ying Wang

Chi-Ying Wang
Research Assistant

Chin Yu

Chin Yu
Associate Professor of Chemistry

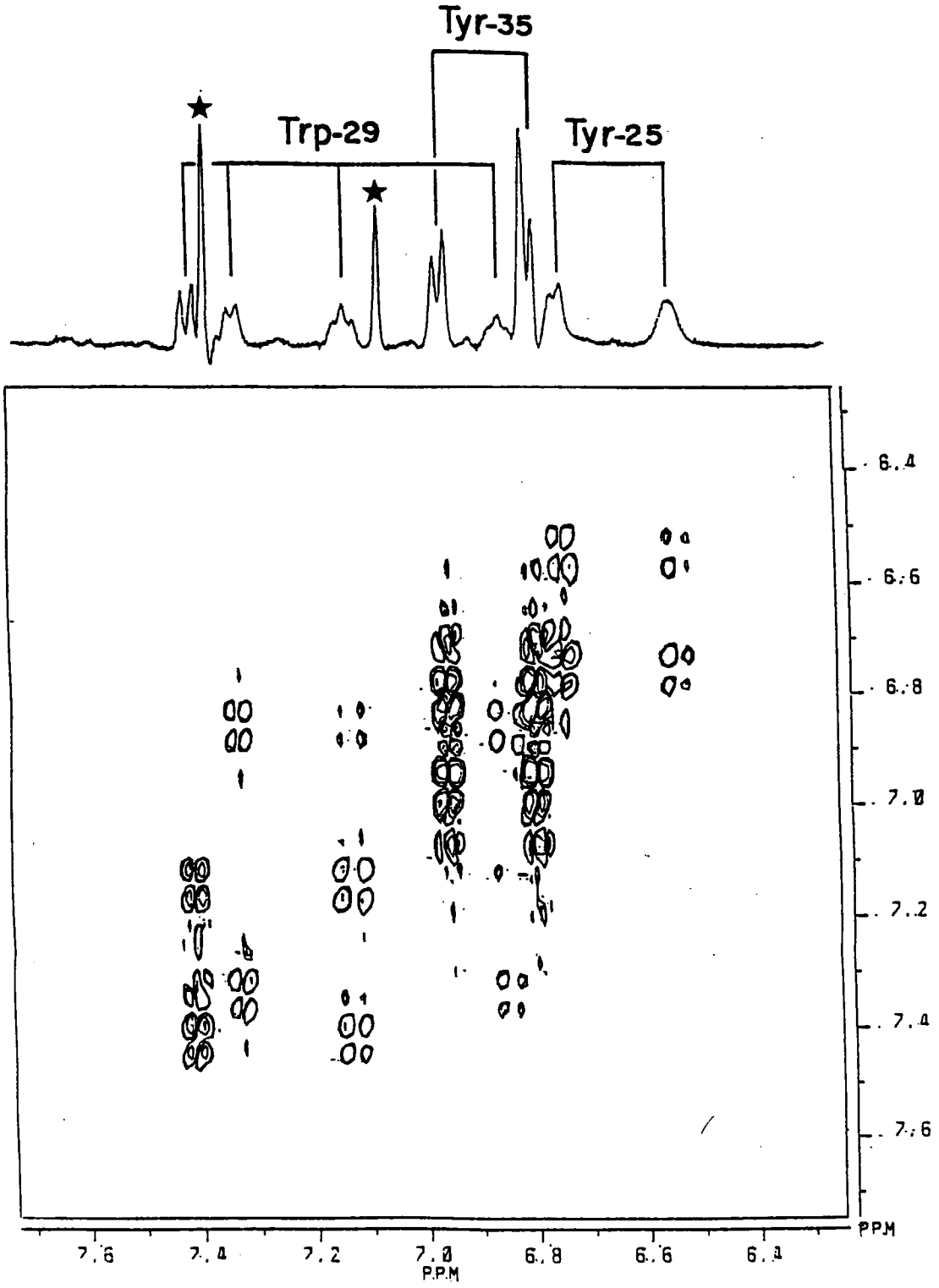


Figure 2QF-COSY Spectrum of cobrotoxin of aromatic region

355-78

Wilton Materials Research Centre

PO Box No 90 Wilton Middlesbrough
Cleveland TS6 8JE England
Telephone Eston Grange (0642) 454144 (Switchboard)
Eston Grange (0642) 43 (Direct Line)
Telex 587461 ICI WWC G
Cables ICI Wilton Middlesbrough
Facsimile (0642) 432 444

Professor B L Shapiro
966 Elsinore Court
Palo Alto
California 94303
USA

Your ref	Our ref	Tel ext	Date
	NJC/LL	2147	8 March 1988 (received 3/19/88)

Dear Professor Shapiro

WHY TWO-DIMENSIONAL NMR?

An attractive feature of two-dimensional NMR plots is their ability to convey an impression of sophistication in an NMR experiment. Gone are one-dimensional spin decoupling and nuclear Overhauser experiments to be replaced by the COSY and NOESY experiments with the seemingly complex contour or stacked plots. Of course two-dimensional experiments can be more efficient methods of obtaining spin and spatial connectivities but how often are the data fully analysed to realise this advantage?

None of us are above the desire to produce an attractive data set, particularly for the consumption of managers and supervisors. Take as an example determining the rate of a chemical exchange process. Doesn't the contour plot of the chemical exchange caused by ring flipping in 1,4 diphenoxybenzene, Figure 1, look better than the equivalent spectrum using a one-dimensional analogue? But which is a more efficient use of spectrometer time, why the one-dimensional experiment. In the time required to acquire the 2D data for one mixing time, eight one-dimensional experiments can be performed with a better signal-to-noise ratio allowing the rate constant of $27s^{-1}$ to be derived.

I raise this issue merely to suggest some thought be given to the purpose of the two-dimensional experiment. Or is this simply envy, since my two-dimensional plots rarely have off-diagonal peaks?

Nigel Clayden

N J CLAYDEN
Spectroscopy Group
Room D115
Wilton Centre

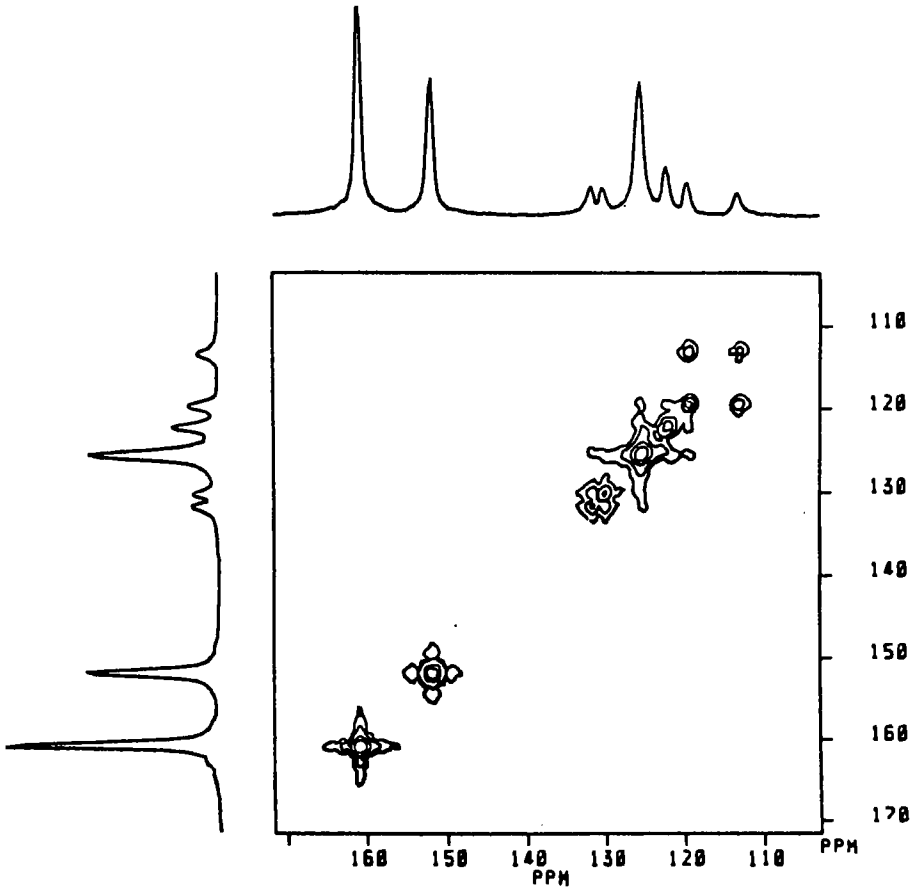
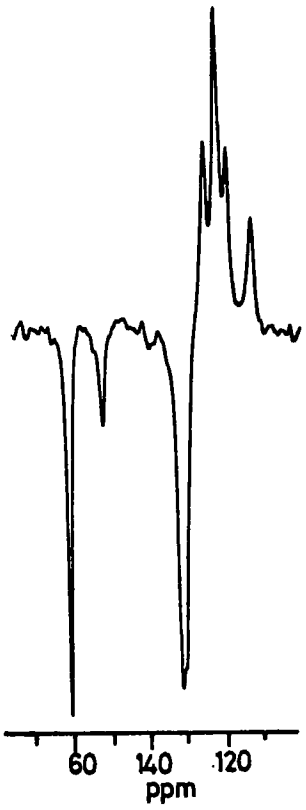


FIGURE 1: 2D Exchange ^{13}C CP MAS NMR spectrum of 1,4 diphenoxybenzene at 294K with a mixing time of 50ms.

FIGURE 2

One dimensional exchange ^{13}C CP MAS NMR spectrum of 1,4 diphenoxybenzene at 294K with a 50 ms mixing time



Dr. V. Wray
GBF Mascheroder Weg 1 D - 3300 Braunschweig

Dr. B. L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court

Palo Alto California 94303
U.S.A.

GBF
Gesellschaft für
Biotechnologische
Forschung mbH

Abteilung
Molekulare
Strukturforschung

Ihre Zeichen	Ihr Schreiben vom	Unsere Zeichen	Telefon	Telex	Datum
		Wr/ud	(05 31) 61 81 - 0	9 526 67 gebio d	11.3.1988
			Durchwahl 353	Telefax (05 31) 6181 515	(rec'd. 3/18/88)

Transferred nOe's in flavonoid systems

Dear Dr. Shapiro,

We have been collaborating recently with Dr. Proksch of the Department of Pharmaceutical Biology of the Technical University of Braunschweig on the structure elucidation of a multitude of methoxyl substituted flavonoids. Although these compounds appear simple the actual determination of the substitution pattern is often no trivial matter. An observation that has proved helpful is that transferred nOe's can be observed when spectra are run in dry DMSO-d_6. Although this phenomenon has been described in a standard text (J.K.M. Sanders and B. Hunter, "Modern NMR Spectroscopy" OUP 1987, p. 229) I cannot remember seeing any useful examples. I, therefore, proffer an example here.

Shown is the ^1H nOe difference spectrum of 6-methoxyluteolin obtained upon low power irradiation of the signal at 3.4 ppm. Transfer of saturation from this signal to the other slowly exchanging OH signals occurs, which in turn lead to positive nOe's for protons adjacent to these groups. Thus null signals are observed for H-6' and H-3, which allows a ready distinction between the latter and H-8. A similar result is obtained if the low field hydroxyl signals are irradiated.

Yours sincerely,

Victor Wray

(Dr.) Victor Wray

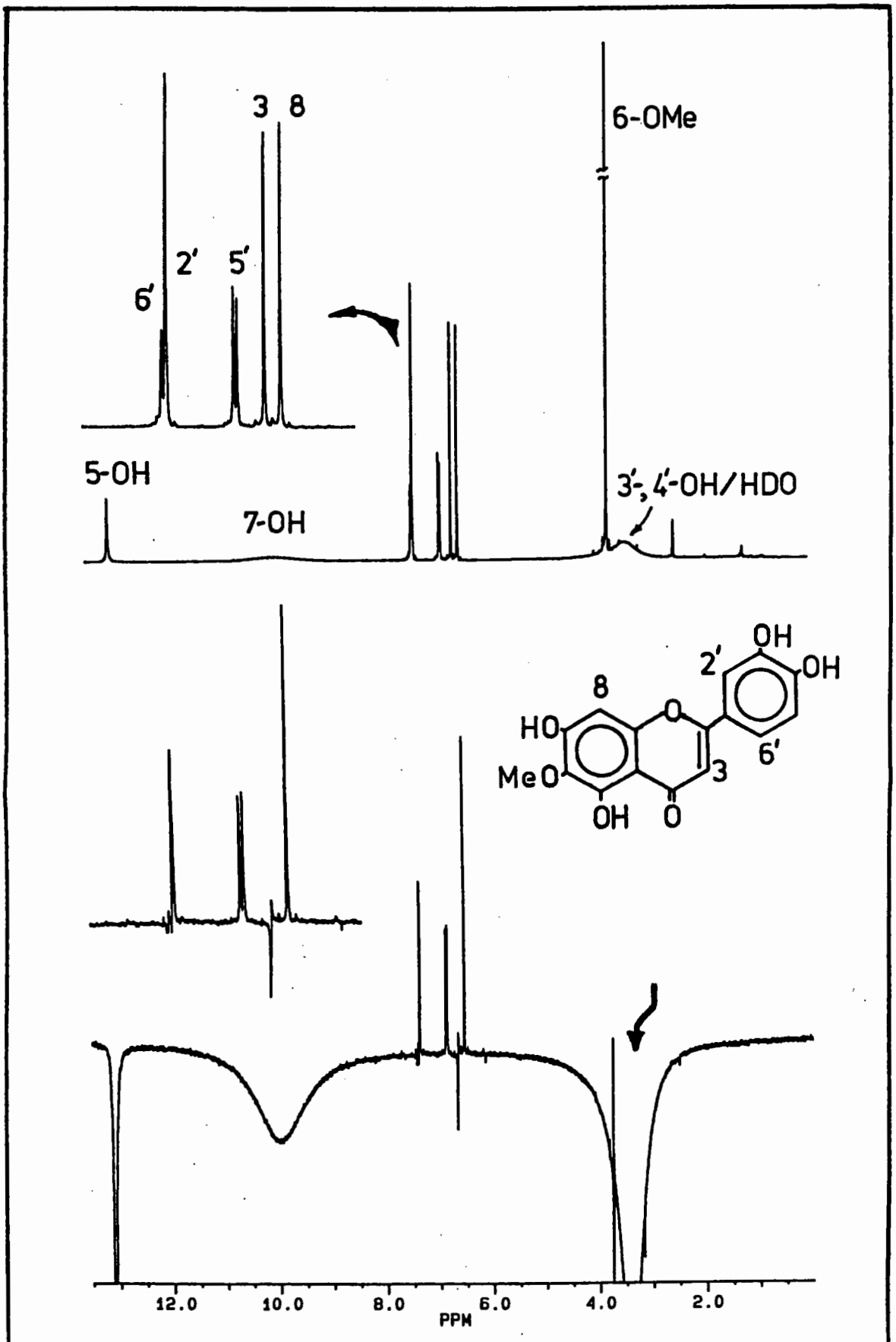


Figure. Normal ^{1}H spectrum of the flavone in dry DMSO-d_6 (top) and nOe difference spectrum after irradiation at 3.4 ppm (bottom).

355-82

MINISTRY OF FORESTRY

WOOD TECHNOLOGY DIVISION
FOREST RESEARCH INSTITUTE
Postal Address: Private Bag, Rotorua
Telegraphic Address: 'Frestra' Rotorua, N.Z.
Telex: NZ21080
Telephone: (073) 475-899 Fax: 479-380

14/5/4/11
IS:WS

7 March 1988

Dr Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto
California 94303
UNITED STATES OF AMERICA

Dear Dr Shapiro

WOOD EXTRACTIVES ANALYSIS BY QUANTITATIVE ^{13}C NMR SPECTROSCOPY

Apologies for the late payment of our subscription. Our newsletters seem to have been taking some time to reach us, coming over here by seamail, back to the States and eventually back to us again. We thought this was all sorted out, but no, our overdue subscription reminder arrived via Jakarta, Indonesia.

Due to our interest in wood extractives, materials which can be extracted from wood with organic solvents, and their effects on the production and properties of mechanical pulps we required a quick method for analysing softwood extractives. The existing method, while giving good accurate results, is very time consuming to carry out taking of the order of 2 days per analysis.

Wood extractives contain a large number of compounds but may be conveniently grouped into four classes: free fatty acids; diterpene resin acids; fatty acid triglycerides; and unsaponifiables, a diverse group of compounds containing diterpene alcohols, hydrocarbons and sterols. We have found that in deuterochloroform the carbonyl carbons of fatty acids, resin acids and fatty acid esters appear at different places in the carbon spectrum. Hence by running the ^{13}C NMR spectrum quantitatively in the presence of a suitable internal standard (vanillin) it was possible to determine the amounts of fatty acids, resin acids and fatty acid esters in an extractives sample with an accuracy comparable to that of the classical procedure.

The T1's of the three carbonyl carbons were measured and found to range from 1 - 3s. The spectra were acquired with a repetition time of 15 s, a flip angle of close to 90° and broad band proton decoupling only during carbon signal acquisition.

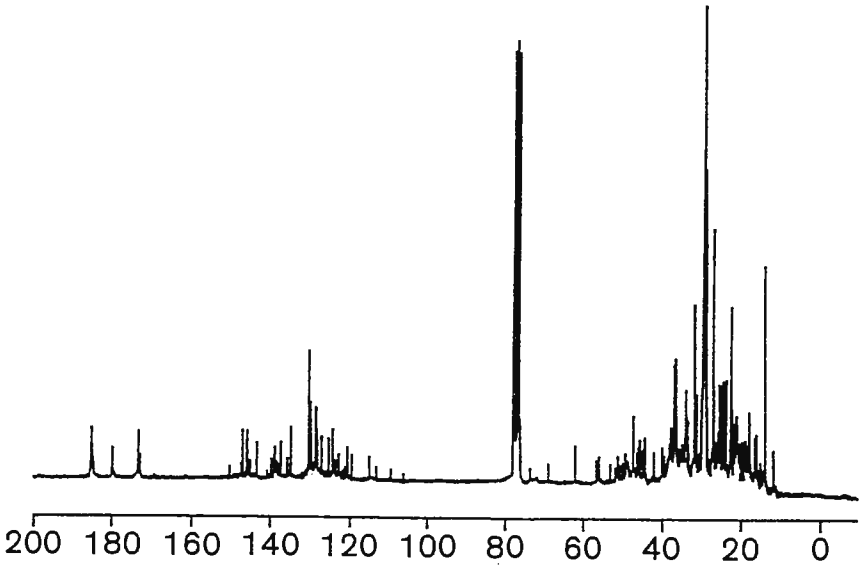
Using this method we have found that wood extracts often contain significant amounts of fatty acid esters other than triglycerides so it is better to use the integral over the glycerol part of the triglyceride to determine these esters - this assumes that no di- and monoglycerides are present in the sample. An estimate may also be made from the spectrum of the amounts of other fatty acid esters present in the sample.

This method is now routinely used at our Institute. Sample sizes range from 1.5 g (2 h/analysis) to100 mg (overnight), and smaller samples if we could be persuaded to use the spectrometer to run them.

Yours sincerely

R. Meder

Ian D. Suckling



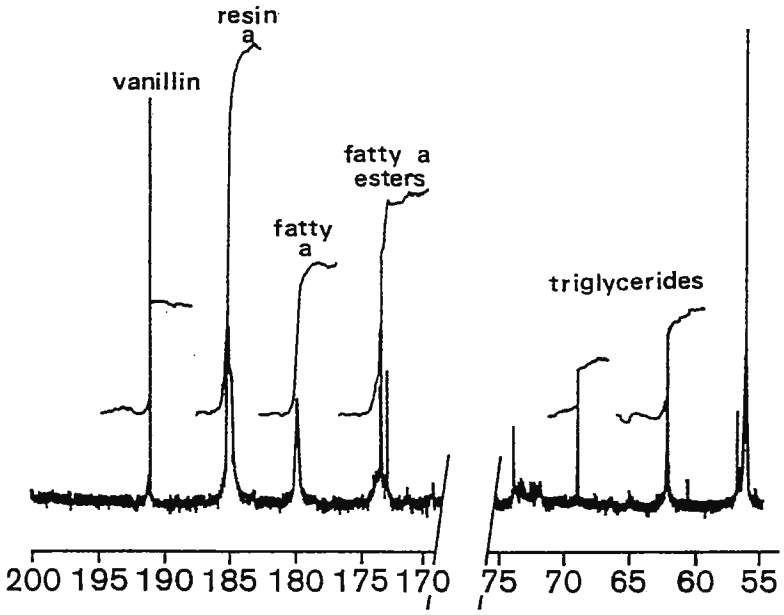


Fig. 1 Quantitative spectrum of a Pinus radiata dichloromethane wood extract.

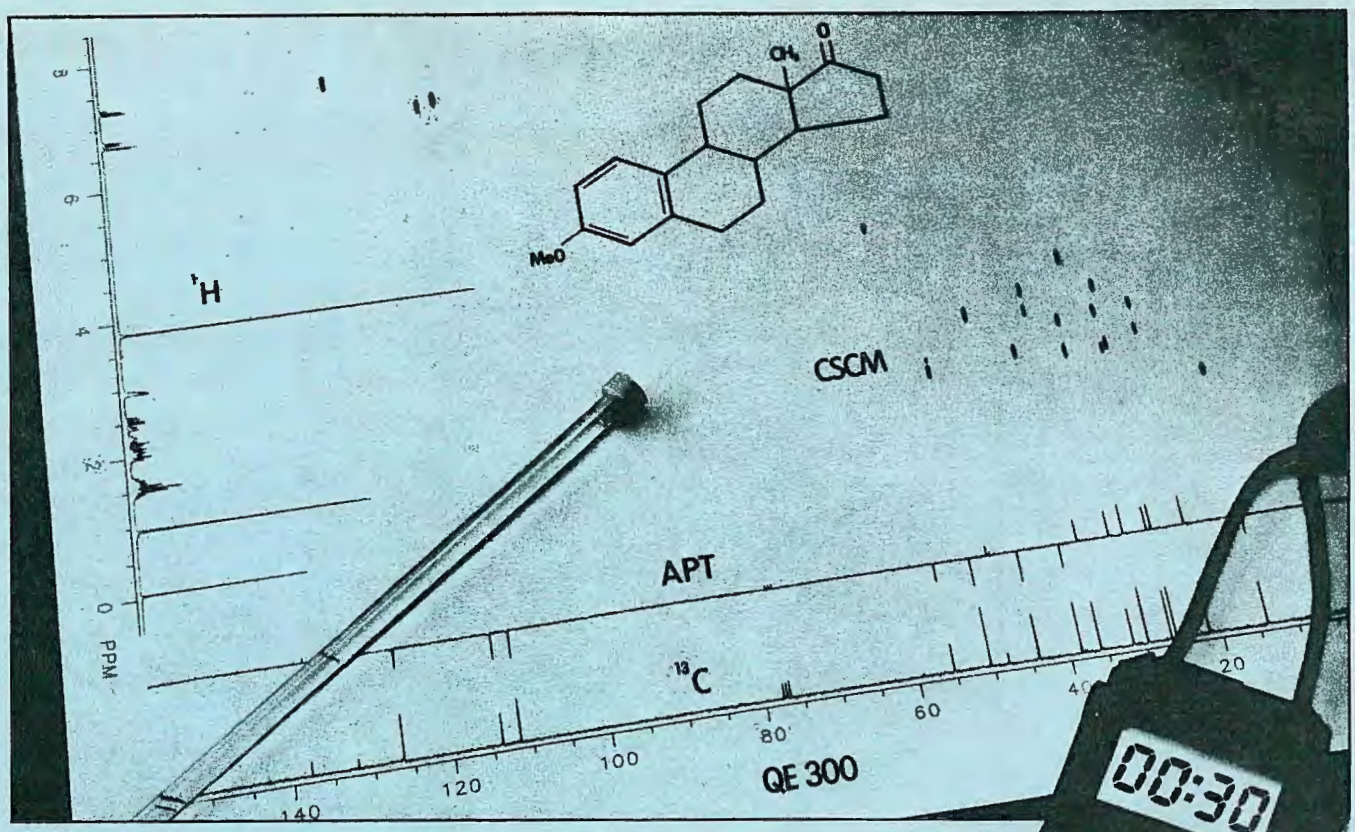
Fig. 2 Expansion showing the carbonyl and glyceride regions from the spectrum of the same sample rerun with the addition of vanillin, the internal standard.

TEXAS A&M UNIVERSITY
NMR NEWSLETTER

No. 355
April 1988

Table of Contents, cont'd.

* * * * *



GE Performance!

^{1}H, ^{13}C, APT, and 2D NMR in ½ hour - automatically!

The GE QE-300 does it all – faster than any other NMR spectrometer.

A ^{1}H spectrum, ^{13}C spectrum, an attached proton test (APT), and a ^{1}H-^{13}C chemical shift correlation map (CSCM). All these analyses can be performed in as little as ½ hour, on as little as 50 mg. of sample, for most organic compounds. And the QE-300 does them all – automatically.

With the NMR industry's most advanced automation.

This performance is made possible by the QE-300's automated software, hardware, and powerful MACRO programming capability.

Set-up starts with *Autolock*. Lock on as little as 10% $CDCl_3$ in a 5 mm tube.

Use *Compushim* for touching-up spinning shims or complete shimming with both spinning and non-spinning gradients using the lock signal or observe FID.

Autogain optimizes the receiver gain independently for sequential ^{1}H and ^{13}C acquisition.

After data acquisition, *Autophase* accurately phases ^{1}H and ^{13}C spectra.

And finally, the analysis is completed with *Autointegrate*.

All these routines can be called up from QE-300 MACROs. In fact, any QE-300 operation, including pulse programs, can be implemented via MACROs for automatic, unattended sample analysis.

And the most complete package of hardware accessories.

The QE-300 is available with the industry's most reliable, highest capacity (100 positions!) *Automatic Sample Changer*. Plus, you can add an array processor, a variety of hard disks, and switchable probes for even higher sample throughput and performance.

Structural elucidation simplified.

For many organic molecules, the four experiments presented above will be all you need to determine or confirm molecular structure. For more complex applications, GE/NMR offers an extensive ^{13}C library with outstanding search capability. This library contains data from over 10,000 compounds and is currently being expanded using a QE-300 in operation at the Aldrich Chemical Company.

High throughput and performance demonstrated.

Get all the facts on the GE/NMR QE-300. Better yet, arrange for a demonstration. Call the GE/NMR group at (415) 490-8310. Or write General Electric Company, NMR Instruments, 255 Fourier Avenue, Fremont, CA 94539.

GENERAL ELECTRIC

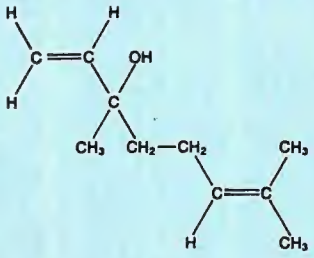
JEOL'S GX-FT NMR Systems

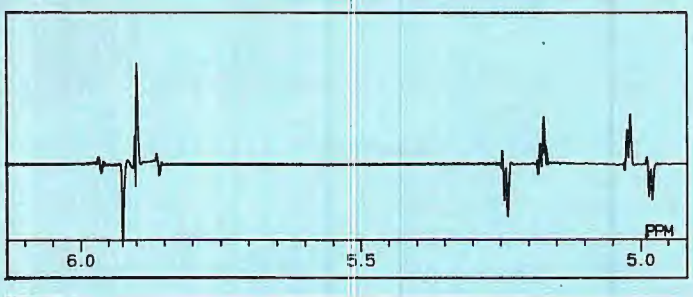
Subject: Automation

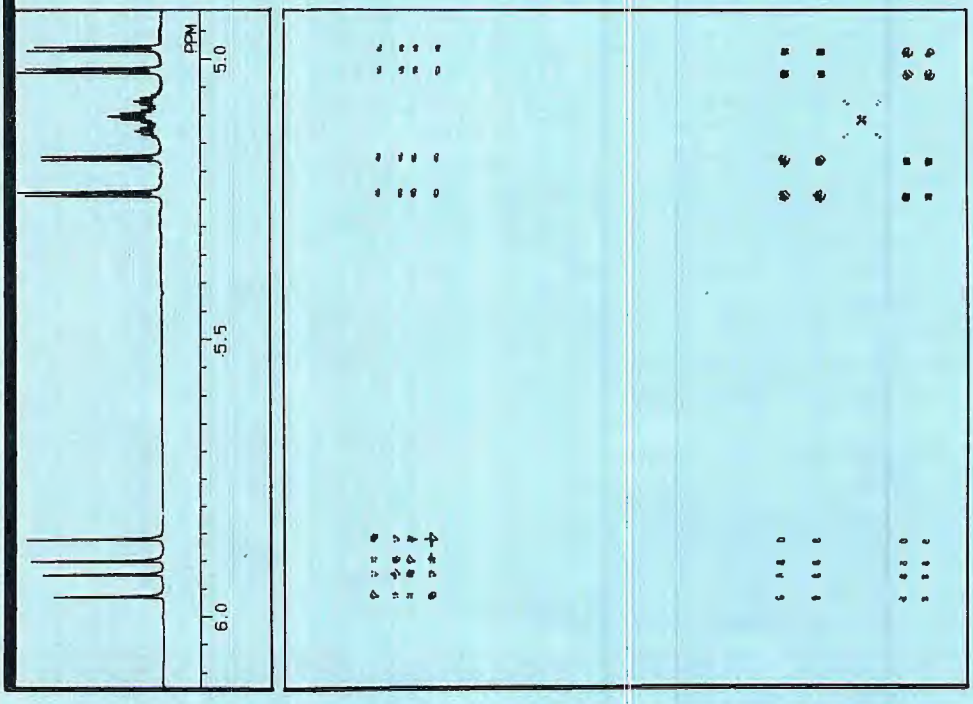
One of the more than 200 (and growing) automated routines available on the GX-Series; the data illustrates a Double Quantum Filter Phase Sensitive Cosy on the downfield section of Linalool run on a GX-270/WB (89mm) MHz spectrometer. From the moment you load the sample, spinning, lock, shimming, acquisition, transform, phase correction, and plotting are totally automated. Should you need something not already in our menu a few strokes on the keyboard will put it there.

So whether your requirements are for routine or research, the GX-FT NMR is an instrument that you should consider when evaluating FT-NMR Systems.

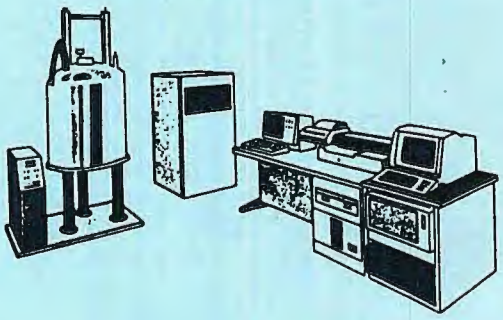
Linalool







The GX Series FT-NMR Spectrometer



For further information call:

JEOL

Serving Advanced Technology

11 Dearborn Road, Peabody, MA 01960
(617) 535-5900