TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 413

February 1993

Continued on Inside Back Cover

Meet us in St. Louis...

Hospitality Suite - ENC 1993

CAMBRIDGE ISOTOPE LABS

invites you to stop by our hospitality suite to
discuss the latest products and applications in NMR spectroscopy.
CIL is proud to offer products unavailable anywhere else...

CIL ACQUISITION OF MSD INVENTORY!

Our inventory is now bigger than ever with the addition of MSD Isotopes' inventory and assets purchased this January. CIL is proud to supply its customers with the largest inventory of stable isotopically labeled compounds, including many unique compounds previously available only from MSD.

BIOLOGICAL NMR PRODUCTS

- **Crystalline Amino Acids**
  CIL offers the largest selection of isotope labeled amino acids, including (U-13C, 15N), (13C), and (15N) crystalline amino acids
- **Custom Amino Acid Mixtures for Mammalian Cell Systems**
- **Algal Lyophilized Cells**
- **Algal Whole Hydrolysates**
- **Algal Amino Acids Mixtures**

NEW Octapeptide Standard for Triple Resonance NMR

CIL has developed the first commercially available isotope labeled peptide reference standard for NMR spectroscopy experiments:

H-Tyr-Gly-[15N, 13C] Gly-[15N, 13C] Phe-[15N, 13C] Leu-Arg-Arg-Ile-OH

WHERE: Directors Row 43
Adams Mark Hotel

WHEN: March 14, 15, 16, & 17
7-12 midnight

If you won't be at ENC this year,
please call to request literature on any of the above products.

CIL

CAMBRIDGE ISOTOPE LABORATORIES
20 Commerce Way, Woburn, Massachusetts

1-800-322-1174 or 617-938-0067 617-932-9721 (fax) 800-643-7239 (Canada)

TEXAS A&M NMR NEWSLETTER NO. 413, FEBRUARY 1993

AUTHOR INDEX

TEXAS A&M NMR NEWSLETTER NO. 413, FEBRUARY 1993

ADVERTISER INDEX

SPONSORS OF THE TAMU NMR NEWSLETTER

Abbott Laboratories
American Microwave Technology
ATI Instruments
Bruker Instruments, Inc.
Burroughs Wellcome Co.
Cambridge Isotope Laboratories, Inc.
Chemagnetics
Cryomagnet Systems, Inc.
The Dow Chemical Company
The Du Pont Merck Pharmaceutical Company
Eastman Kodak Company
E. I. du Pont de Nemours & Company
JEOL (U.S.A.) Inc., Analytical Instruments Division
The Lilly Research Laboratories, Eli Lilly & Company
Merck Research Laboratories
Millipore Corporation, Waters Chromatography Division
The Monsanto Company
Nalorac Cryogenics Corporation
Norell, Inc.
Oxford Instruments
Petroleum Recovery Institute
The Procter & Gamble Company, Miami Valley Labs
Programmed Test Sources, Inc.
Shell Development Company
Tecmag
TRIPOS Associates/New Methods Research, Inc.
Unilever Research
Union Carbide Corporation
The Upjohn Company
Varian, Analytical Instrument Division

Welcome to this new Sponsor!

FORTHCOMING NMR MEETINGS

International Symposium on Solid-State NMR Spectroscopy of Polymers, Keystone, Colorado, **February 28 - March 3, 1993**; Contact: Barbara D. Hogan, Du Pont, CR&D, P. O. Box 80356, Wilmington, Del. 19880-0356; Phone: (302) 695-4394; FAX: (302) 695-8207.

PITTCON'93, Atlanta, Georgia, **March 8-12, 1993**; Contact: Dept. 60, Suite 332, Penn Center Blvd., Pittsburgh, PA 15235-5503; Phone: (412) 825-3220, Toll-free: 1-800-825-3221; Fax: (412) 825-3224.

1993 Keystone Symposia on Molecular & Cellular Biology, Taos, New Mexico: **March 8-14, 1993**, *Frontiers of NMR in Molecular Biology - III*; Organizers: T. L. James, S. W. Fesik, and P. E. Wright; Information: Keystone Symposia, Drawer 1630, Silverthorne, CO 80498; Telephone: (303) 262-1230.

In Vivo Magnetic Resonances Spectroscopy VI. Symposium on *In Vivo* Magnetic Resonances Spectroscopy: Focus on Spectroscopic Techniques, St. Louis, Missouri, **March 13-14, 1993**; Contact: Radiology Postgraduate Education, Room C-324, University of California School of Medicine, San Francisco, CA 94143-0628; Phone: (415) 476-5808; Fax: (415) 476-9213.

34th ENC (Experimental NMR Conference), St. Louis, Missouri, **March 14-18, 1993**; Contact: ENC, 815 Don Gaspar, Santa Fe, New Mexico 87501; Phone: (505) 989-4573; Fax: (505) 989-5073. See TAMU NMR Newsletter 408, 45.

Advanced School on Magnetic Resonance and Protein Dynamics, Erice, Sicily, Italy, **March 15-21, 1993**; Contact: Prof. Oleg Jardetzky or Stanford Magnetic Resonance Lab., Stanford Univ., Stanford, CA 94305-5055; Fax: (415) 723-2253; See TAMU NMR Newsletter 411, 50.

High Resolution NMR Spectroscopy (a residential school), University of Sheffield, England, **April 19-23, 1993**; Organizer: Dr. B. E. Mann (Sheffield); For information, contact Ms. L. Hart, The Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, England; Tel.: 071-437-8656.

Gordon Research Conference: Magnetic Resonance, Wolfeboro, NH, **July 11 - 16, 1993**; Contact: Dr. A. M. Cruickshank, Gordon Research Center. University of Rhode Island, Kingston, RI, 02881-0801; (401) 783-4011 or -3372; FAX: (401) 783-7644.

35th Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado: **July 25-29, 1993**; Contact: Patricia L. Sulik, RML, Inc., 456 S. Link Ln., Ft. Collins, CO 80524; Phone: (303) 530-1169.

12th Annual Scientific Meeting and Exhibition of the Society of Magnetic Resonance in Medicine, New York, NY, **August 14-20, 1993**; Contact: SMRM, 1918 University Ave., Suite 3C, Berkeley, CA 94704; Phone: (510) 841-1899; FAX: (510) 841-2340.

1993 FACSS Meeting, Detroit, Michigan, **October 17-22, 1993**; Contact: H. N. Cheng, Hercules, Inc., Research Center, 500 Hercules Road, Wilmington, DE 19808; Phone: (302) 995-3505; Fax:. (302) 995-4117. See TAMU NMR Newsletter 411, 10.

Additional listings of meetings, etc., are invited.

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

CSIRO Division of
Chemicals & Polymers
Private Bag 10,
Victoria 3168
Australia.
21 December 1992
(received 12/29/92)

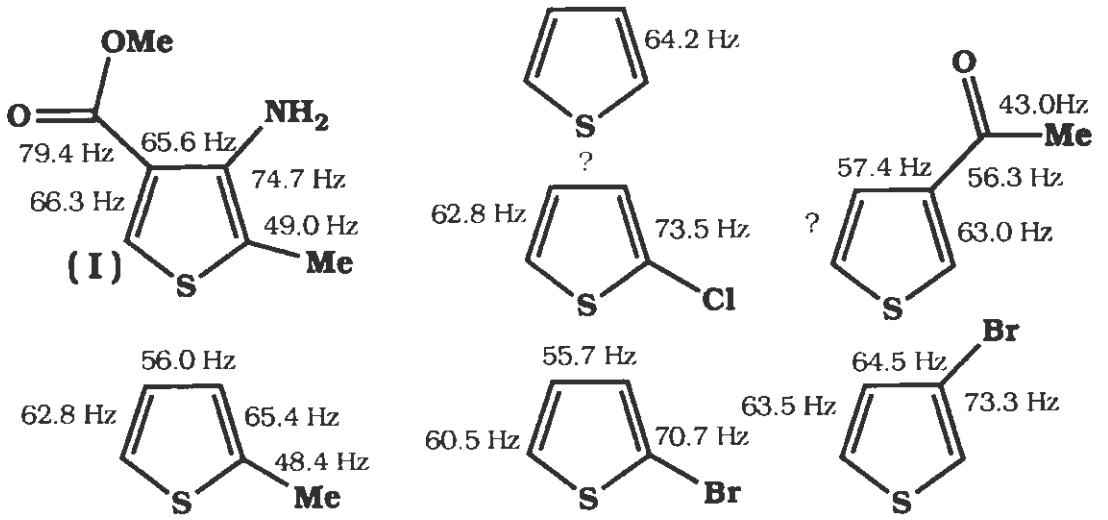
Dear Dr. Shapiro,

Carbon - Carbon Coupling Constants of Thiophenes

Recently we had a carbon chemical shift assignment problem in the spectrum of a tri-substituted thiophene **(I)**. It was getting rather late in the day and a quick examination of the various long-range J_{CH} of the carbon proton-coupled spectrum did not resolve the shift ambiguity. We chose to resolve the problem overnight by using a 1D INADEQUATE experiment and so confirm the shift assignments via the J_{CC} couplings.

This settled the assignment ambiguity but much to our surprise yielded a thiophene ring J_{CC} of approximately 75 Hz **(I)**.

Since then we have searched the chemical store for other substituted thiophenes and now have data for 9 compounds. Generally thiophenes are hard to come by, especially amino thiophenes.



The data suggest that a hetero-atom substituent on the ring increases the magnitude of the carbon- carbon coupling (Cl>Br) as observed in benzene analogues. The role of an amino group on J_{CC} is still being investigated as there are some odd J_{CC} values in **(I)** . It was not possible to obtain all the J_{CC}'s with the INADEQUATE experiment for some compounds. This occurred where the carbon chemical shifts were approaching magnetic shift equivalence at our field strength of 5.87 T.

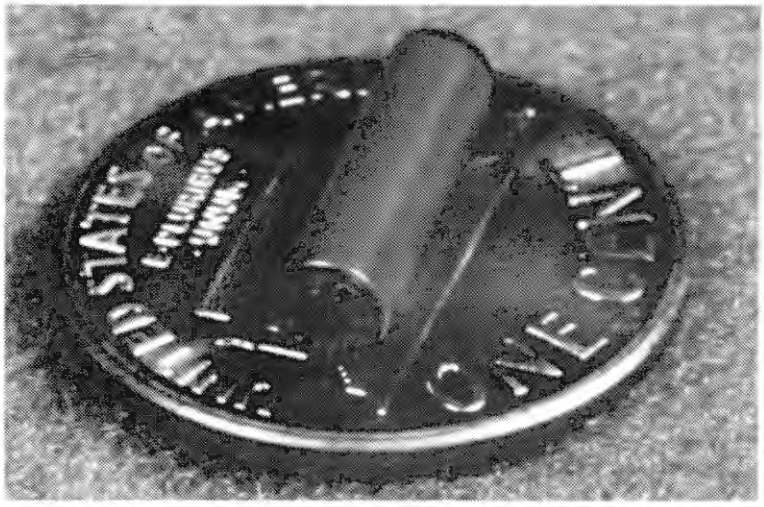
Norman. S. Ham

R. Ian. Willing

Please credit this contribution to Prof. I.D. Rae's subscription.

What's faster than high speed? Supersonic MAS!

For ten years Doty Scientific has led the field in high speed sample spinning. Our supersonic spinner systems use a unique air bearing design (patent pending) for highest stability, radial-inflow microturbines (patent pending) for highest efficiency, and cooled bearing gas to keep the sample temperature constant.



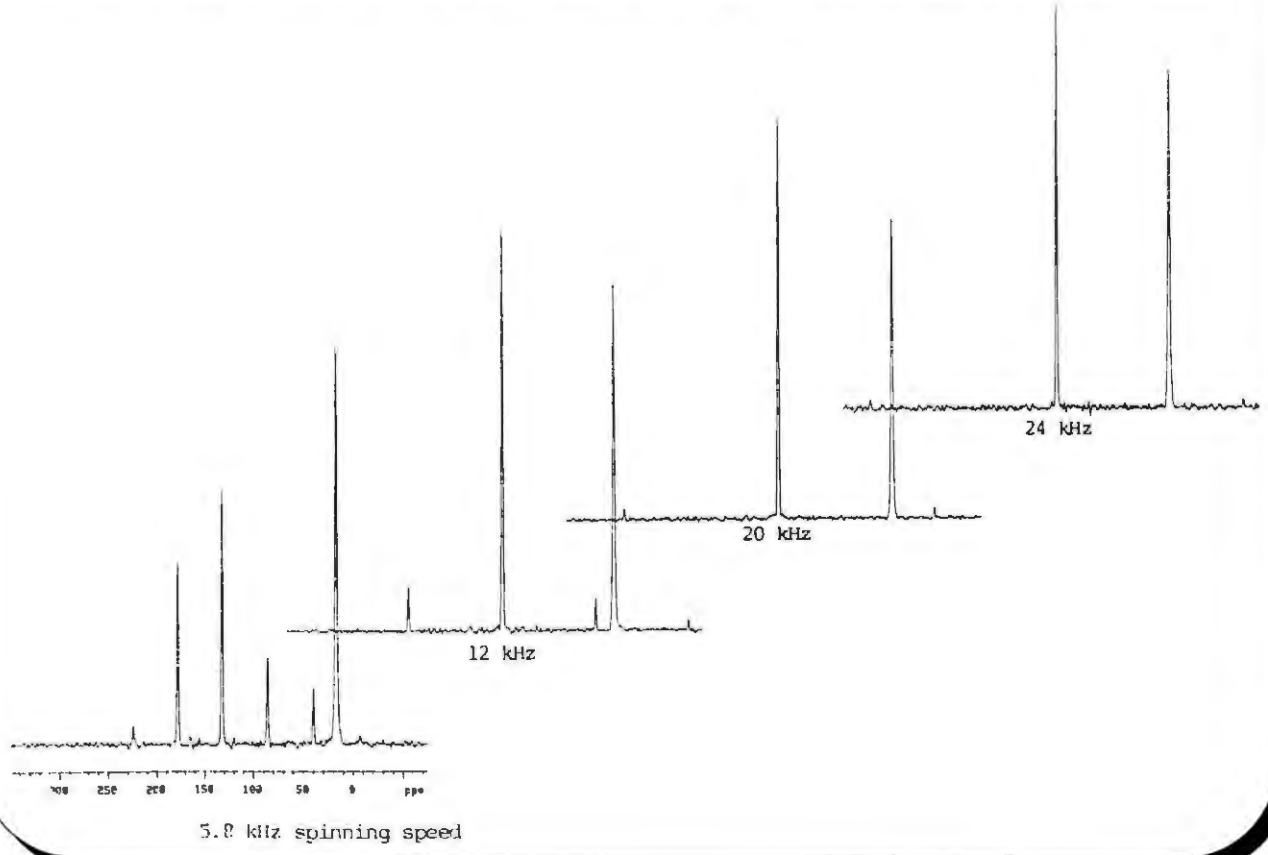
3.5-mm SUPERSONIC CP/MAS

Spinning speed - 26 kHz
Sample volume - 20 µl to 30 µl

The 3.5-mm supersonic spinner is available for probes 30.5 mm in diameter and larger.

Applications for ^{1}H, ^{19}F and quadrupolar nuclei.

This Hexamethylbenzene spectrum at a series of spinning speeds was obtained on a Varian narrow bore Unity 500 MHz Spectrometer, using a Doty 3.5 mm Supersonic MAS Probe. The probe is single-tuned with a multinuclear observe channel.
The spectra was provided by the Varian applications lab in Palo Alto and Dr. Laima Baltusis.



Doty Scientific, Inc. 700 Clemson Road, Columbia, SC 29223 USA Phone: (803) 788-6497 Fax: (803) 736-5495

Doty High Resolution Liquids Probes

Our versatile NMR probes can supply the scientist with tools for the latest experimental techniques, even something really unique like a 4 μs t_{90} for protons at 500 MHz. (You might also be interested in our new line of PFG and MRI probes.)

- **Double-, Triple-, or Quad-tuned**
- **Multinuclear Tuning Options**
- **Inverse Detection Probes**
- **Water Suppression**
- **Standard VT range:** -100° to +140°C

High-Power, Fluorine-Proton Decoupling

Our patented coil design allows large-volume, high-field ^{1}H-^{19}F experiments. Achieving high-power simultaneous decoupling on these closely spaced frequencies is a challenging task, but our double-balanced, inductively-coupled circuit makes user tuning simple. It is possible to decouple or observe either nucleus, with appropriate materials choices.

➢ Double-Tuned, ^{1}H -^{19}F ..... $ 2,000 *

High-Power, Triple-Resonance

We have supplied a number of special triple-resonance probes for both MAS and liquids, including ^{1}H -^{19}F -X, ^{1}H -X-^{15}N, and ^{3}H -^{1}H -^{2}H. Any one channel can be made multinuclear in a wide bore. In most wide bore probes, both the lower and middle channels can be multinuclear.

➢ Triple-Tuned with widely spaced, fixed-frequencies (Such as ^{1}H -^{31}P-^{15}N) ..... 1,800 *

➢ Triple-Tuned Multi-X with well spaced frequencies (^{1}H -^{31}P-X, or ^{1}H -X-^{15}N) ..... 3,500 *

➢ Triple-Tuned Multi-X, close resonances, ^{1}H -^{19}F -X ..... 6,000 *

➢ Triple-Tuned, Double-Multi-X, well spaced (^{1}H-X-Y) ..... 5,500 *

Quad-Tuned Liquids Probes (Such as ^{1}H-^{13}C-^{2}H-^{15}N)

The above liquids probes are, strictly speaking, quadruple-tuned, with the lock being the fourth frequency. A different frequency may be specified for the fourth channel for a typical additional charge of $ 800*. Lock may be added as a fifth channel for $ 4,000* extra.

High-Resolution Probe ..... $ 11,000

-100° to 140°C, 5 mm to 10 mm, ^{1}H decouple, ^{2}H lock, fixed-observe frequency

*** Add to the price of a liquids probe with appropriate specifications.**

(Foreign prices 10% to 15% higher, plus taxes.)

Doty Scientific, Inc. 700 Clemson Road, Columbia, SC 29223 USA Phone : (803) 788-6497 Fax: 803) 736-5495

December 15, 1992
(received 12/19/92)

Professor Bernard L. Shapiro
Texas A&M University NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Improvements to the Magic Angle Hopping Experiment

Dear Barry,

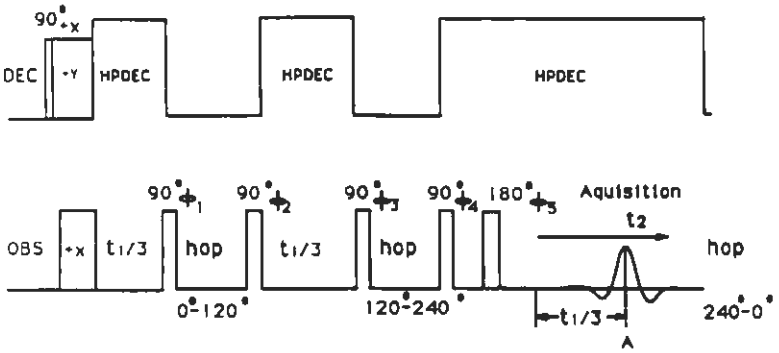
We have recently made several improvements to the Magic Angle Hopping experiment.[1] Using a homemade hopping device coupled to a switched angle spinning controller from Doty Scientific, each 120° sample rotation takes only about 60ms in comparison to the 150ms specified in the original paper. Also, in this variation the data acquisition starts at the beginning of the last one-third of the evolution period rather than at the crystal echo maximum, thus achieving an increase in S/N of about $\sqrt{2}$ over the original experiment. Additionally, the data is acquired in a hypercomplex manner, resulting in a pure absorption phase mode spectrum. The probe built for this experiment also employed a large diameter sample coil (about 4 cm^3), allowing for a typical 2D data set to be acquired in less than 24 hours.

The modified pulse sequence along with the phase cycling is shown below. The experimental ^{13}C powder spectrum for each carbon in 2,6-dimethoxynaphthalene is shown on the next page and the resultant principal values of the ^{13}C shift tensor are listed in Table 1. While we are unable to resolve the signal for $C_{4,8}$ from $C_{4a,8a}$, the two powder patterns are clearly identifialbe in the figure.

Table 1. Principal values of ^{13}C Chemical Shift Tensor in 2,6-dimethoxynaphthalene[a]

assignment	δ_{11}	δ_{22}	δ_{33}	$\delta_{average}$	δ_{MAS}
OCH_3	80	72	11	54	54.1
$C_{1,5}$	177	124	17	106	105.4
$C_{3,7}$	202	132	26	120	119.8
$C_{4,8}$	226	143	22	130	130.6
$C_{4a,8a}$	202	192	-2	131	130.6
$C_{2,6}$	236	163	71	157	156.9

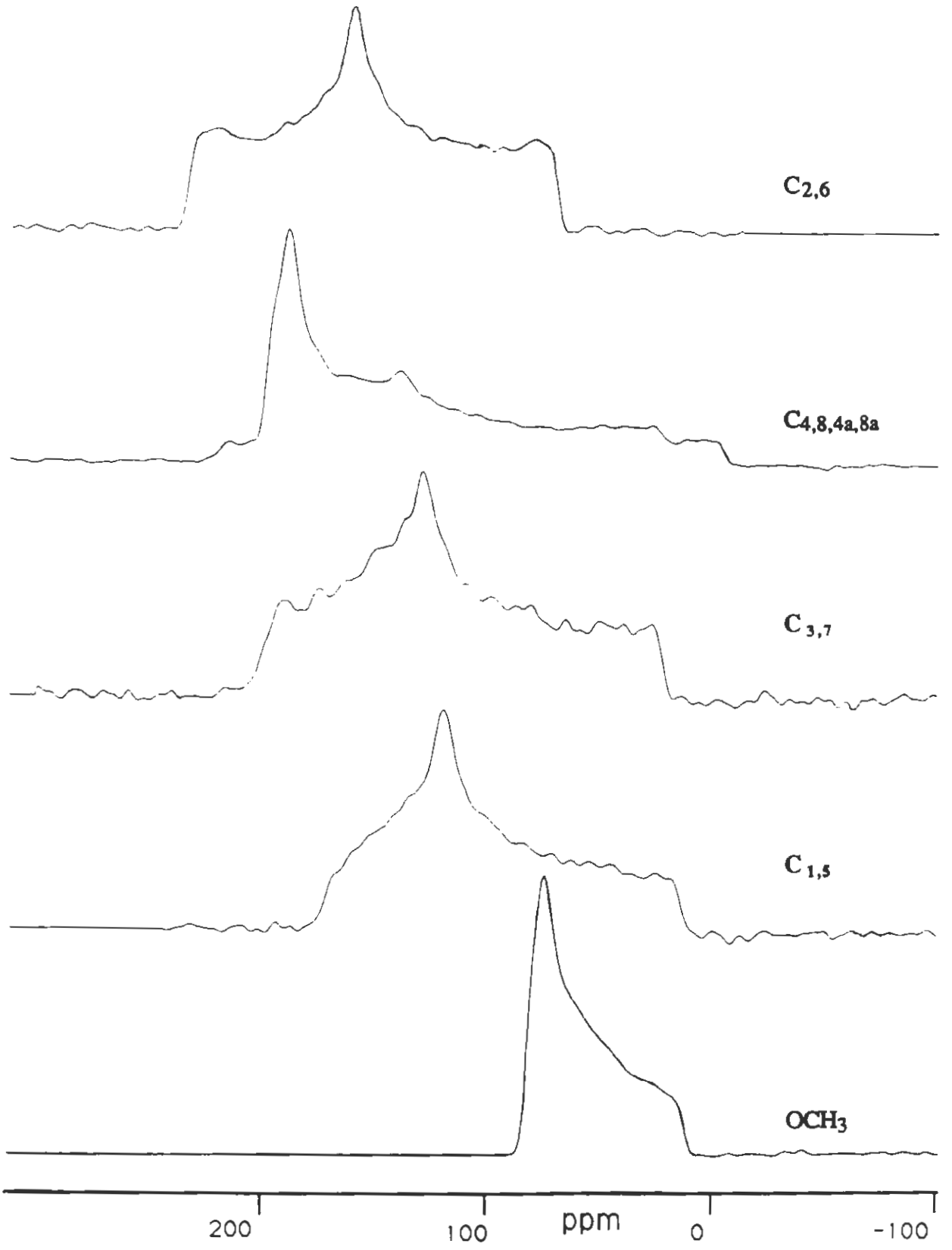
[a] δ values are in ppm with respect to TMS, with an estimated standard deviation ±2ppm.



phase table

step	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	receiver	block
1	+Y	-Y	+Y	-Y	+X	+X	
2	-Y	+Y	-Y	-Y	-X	-X	real
3	-X	-Y	-X	-Y	+X	-X	
4	+X	+Y	+X	-Y	-X	+X	
5	+Y	-Y	-X	-Y	+X	-X	
6	-Y	+Y	+X	-Y	-X	+X	imaginary
7	-X	-Y	+Y	-Y	+X	-X	
8	+X	+Y	-Y	-Y	-X	+X	

[1] A. D. Bax, N. M. Szeverenyi, and G. E. Maciel, J. Magn. Reson. 52, 147 (1983).



Best wishes,

J. Z. Hu

D. W. Alderman

A. M. Orendt

C. Ye

R. J. Pugmire

D. M. Grant

Unocal Science & Technology Division
Unocal Corporation
376 South Valencia Avenue, P.O. Box 76
Brea, California 92621
Telephone (714) 528-7201

Prof. B. L. Shapiro
968 Elsinore Court
Palo Alto, CA 94303

UNOCAL 76

December 10, 1992
(received 1/23/93)

Dear Prof. Shapiro,

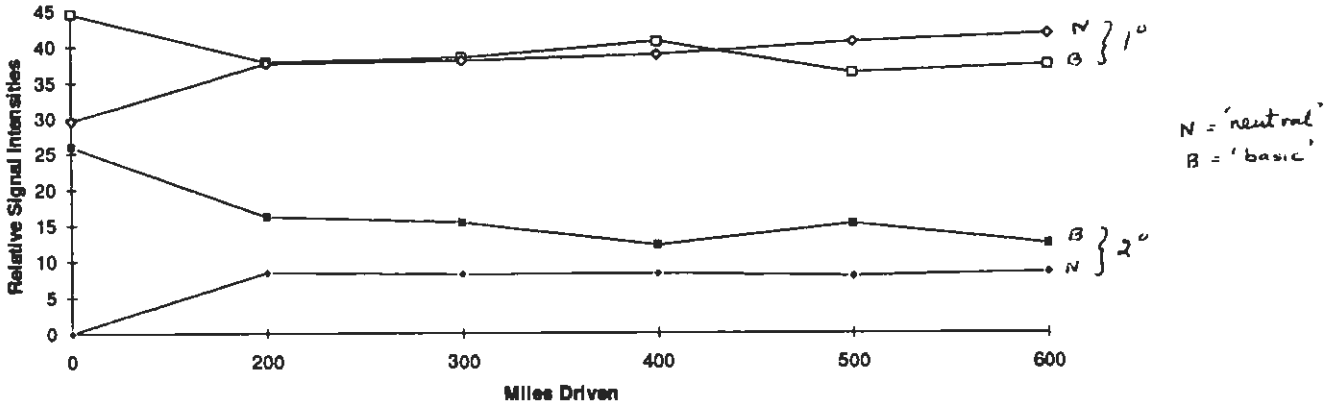
^{31}P NMR Analysis of Racing Engine Oil Additives

Metal dialkyldithiophsphates(DDP) represent one of the largest class of phosphorus containing oil additives. They are used as anti-wear agents, friction modifiers, as well as rust and oxidation inhibitors in industrial and automotive lubricant applications. Zinc(II) derivatives (ZDDP), in particular, are among the most widely used in automotive engine oils and are known to exist in either "neutral" and/or "basic" forms. It has been previously shown (Harrison et. al. *J. Chem. Soc., Dalton Trans.* 807, 1987)that the neutral form is concentration dependent and may exist in equilibrium with the higher oligomeric states. The inter-conversion between these two forms may be represented by the following equation.

$$\underset{\text{"neutral"}}{3\ Zn[S_2P(OR)_2]_2} + ZnO \rightleftharpoons \underset{\text{"basic"}}{OZn_4[S_2P(OR)_2]_6}$$

^{31}P NMR spectroscopy proves to be a valuable tool for their analysis since the chemical shift is quite sensitive to these solution states. The unique ability to ***selectively observe and quantitate*** phosphorus derivatives in the presence of other complex mixtures of compounds typically present in commercial oil formulations is particularly useful. The chemical shift difference between the "neutral" and "basic" form is approximately 4-5 ppm. Furthermore, the observed chemical shift is also sensitive to the nature of the OR moiety. Thus, primary and secondary alcohol derivatives can also be distinguished and quantified. This information is often important in evaluating and predicting the performance characteristics of a given commercial additive package.

An example of its application in monitoring race car engine oil additive performance is shown in the figure below.



The data points represent the average relative signal intensities observed in samples retrieved after various laps. Some of the scatter in the data is due to the fact that although the same Unocal 20W/50 HP(High Performance) racing engine oil was used in all the cars, oil samples from a number of different cars were analyzed. The relative depletion in the basic forms of both "primary" as well as "secondary" ZDDP components is, nevertheless, clearly reflected in the changes observed in the ^{31}P NMR signal intensities . This is attributable, at least partially, to the increased formation of acid by-products resulting from thermal/oxidative degradation of the oil.

Yours Sincerely,

James D. Mercer
Sr. Res. Chemist

Alan D. Denniston
Res. Assoc.

Pradeep Iyer
Sr. Res. Scientist

UNIVERSITY OF CALIFORNIA, BERKELEY

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

NMR Facility *Tel (510) 642-6407 Fax (510) 642-8369*
rnunlist@bloch.cchem.berkeley.edu

COLLEGE OF CHEMISTRY BERKELEY, CALIFORNIA 94720

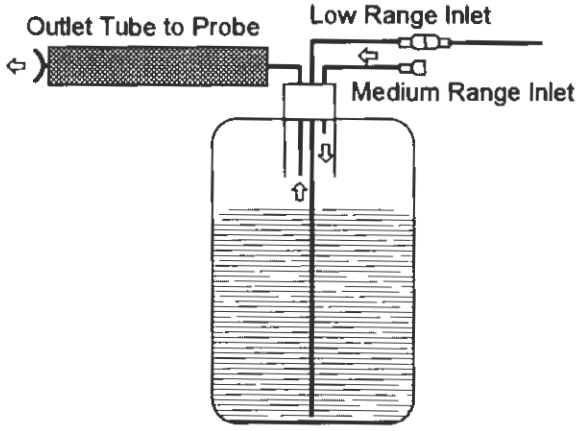
Bruker V.T. Low Temperature Modification.

January 12, 1993
(received 1/21/93)

Dear Barry,

We modified the low temperature V.T. setup on our Bruker spectrometers. The original design uses an evaporator to boil liquid N_2. The gas flow rate is estimated from a front panel evaporator power dial setting. We wanted to be able to have better flow control (high enough to minimize temperature gradients), simpler operation ,and better stability near room temperature. With the evaporator, operation near room temperature proved difficult; adjusting the probe heater and evaporator resulted in either very low flow rate or the temperature was difficult to stabilize.

Our modification provides two operating ranges: A medium range from about -30 ° to +30 °C and a low range from about -100 ° to -30 °C. High temperature operation is unchanged. The new system uses an LN_2 bath and the input nitrogen gas flows either through the liquid (low range) or passes through the cold area above the liquid (medium range). About 6 P.S.I. of inpu pressure is sufficient for flow rates to 500 l/hour. The time to temperature is short; at a gas flow of 400 l/hr it takes about 10 minutes to go from +25° to -35 °C.

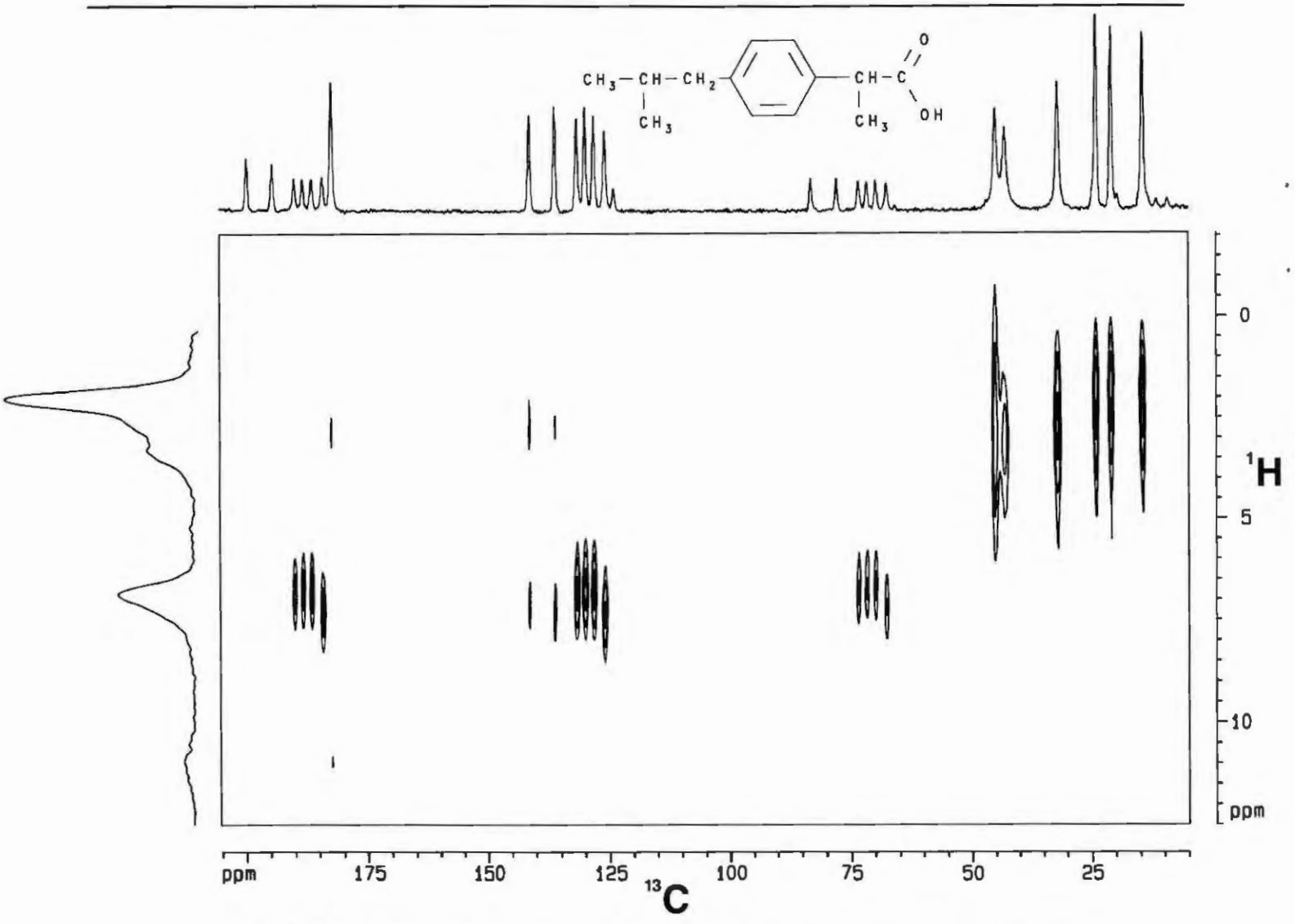


The system uses the Bruker supplied LN_2 Dewar. Stainless steel tubes are attached to a "Quick Flange" of the type as on the evaporator. A 5 P.S.I. relief valve (not shown) is mounted on the same flange. One tube, the Low Range Inlet, reaches to within a few millimeters of the bottom. The medium range inlet tube reaches about 100 mm into the Dewar neck. The outlet tube (polyethylene) reaches past the Dewar neck, about 170 mm. This outlet tube is connected to the probe. Valved (closed while not connected) inline couplers (Cole-Parmer) are used to connect the inlets to the Bruker V.T. gas outlet. The outlet tube is insulated with 1/2 " Armaflex. (A Dewared design could probably extend the low range past -100 °.) Range switching is done by changing the gas inlet. This is possible during operation.

Sincerely,

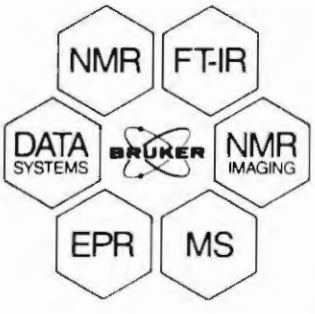
Rudi Nunlist

ASX-Advanced Solids Excellence



Solid State 2D HETCOR of Ibuprofen

In this spectrum the solid state 2D HETCOR experiment, developed in the Bruker applications laboratory, has been applied to the pharmaceutical compound ibuprofen. For comparison, 1D ^{13}C CPMAS and BR-24 ^{1}H CRAMPS spectra are displayed along the axes in place of the usual 2D projections. Strong cross peaks are visible for all of the directly bonded proton-carbon groups, as well as first order sidebands for the four aromatics. In addition, each of the three non-protonated carbons is shown to correlate to at least two long range protons. Note that minute differences in proton chemical shift, impossible to resolve in the 1D CRAMPS spectrum, are clearly visible in the 2D spectrum. 2D HETCOR requires simultaneous, fully windowless pulse sequences to be applied to both protons and carbons during the evolution and mixing periods. All the data shown here was obtained and processed on a Bruker ASX-300.



Australia: BRUKER (Australia) Pty. LTD., Alexandria, New South Wales, Tel. 02-5506422
Belgium: BRUKER SPECTROSPIN S.A./N.V., Brussels, Tel. (02) 648 53 99
Canada: BRUKER SPECTROSPIN (Canada) LTD., Milton, Ontario, Tel. (416) 876-4641
England: BRUKER SPECTROSPIN LTD., Coventry, Tel. (0203) 855200
France: SADIS BRUKER SPECTROSPIN SA, Wissembourg, Tel. (088) 73 6800
India: BRUKER INDIA SCIENTIFIC Pvt. LTD., Andheri (West), Bombay, Tel. 22-62-62-232
Italy: BRUKER SPECTROSPIN SRL, Milano, Tel. 02-70-636-370
Japan: BRUKER JAPAN CO. LTD., Ibaraki-ken, Tel. 0298-52-1234
Netherlands: BRUKER SPECTROSPIN NV, Wormer, Tel. (75) 28 52 51
Scandinavia: BRUKER SPECTROSPIN AB, Täby, Sweden, Tel. (00468) 758-03-35
Spain: BRUKER ESPANOLA S.A., Madrid, Tel. 341-259-20-71
Switzerland: SPECTROSPIN AG, Fallanden, Tel. 1-82 59 111
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. 0421-2205-0
BRUKER-SAXONIA ANALYTIK GMBH, Leipzig, Tel. 003741-239-2453
USA: BRUKER INSTRUMENTS, INC., Billerica, MA 01821, 508-667-9580, Fax 508-667-3954
Regional Offices in Chicago, IL, (708) 971-4300 / Wilmington, DE, (302) 478-8110
Houston, TX, (713) 292-2447 / San Jose, CA, (408) 434-1190

LABORATOIRE DE RÉSONANCE MAGNÉTIQUE NUCLÉAIRE
UNIVERSITÉ CLAUDE BERNARD LYON I

Bâtiment 721
43, boulevard du 11 Novembre 1918
69622 Villeurbanne Cedex
Tél. 72.44.82.67 - Secr. 72.44.80.84
Fax (33) 72.44.81.99

Professor SHAPIRO
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

(received 12/29/92)

About Backprojection imaging

An increasing interest is today becoming in fast MRI in vivo, and in the field of materials with a short relaxation behaviour such as porous media. An early technique known as "Backprojection imaging" can be revisited to implement some aspects of this problem.

This method needs a gradient field, the direction of which is incremented by steps in two directions of the so-called Euler angles Θ and Φ, the module being constant. A further software reconstruction in 3D is then possible with off-line techniques. The 3 components of the gradient field are respectively proportionnal to $\sin\Theta\cos\Phi$, $\sin\Theta\sin\Phi$, $\cos\Theta$.

Such a configuration can be developed using "TOMIKONN" software from Brüker, wich gives in a special mode of gradient programming ("Mode D") output voltages following these expressions, but the values are maintained during the whole elementary sequence, including the RF pulse.

We developed here (next page) an electronic unit located between the converter output and the power gradient supply. It is claimed to give :

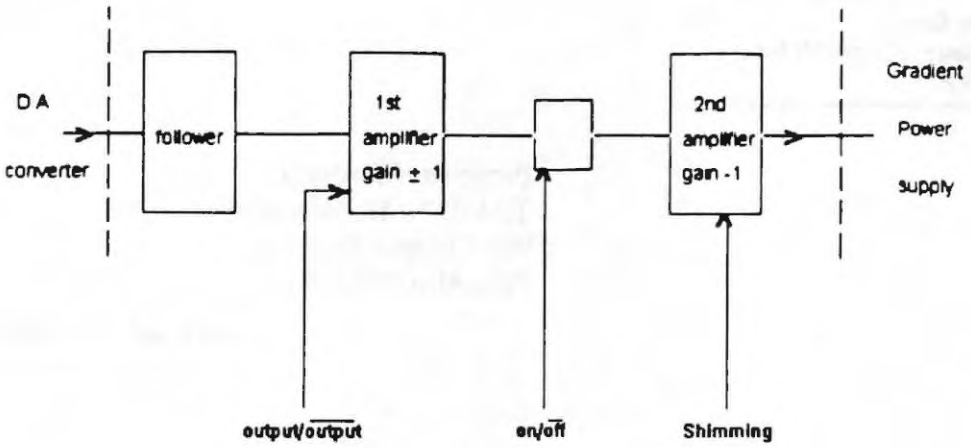
i) either null either the output voltage
ii) the output or its reversal

Two logic commands (labeled ON/$\overline{\text{OFF}}$ and OUTPUT/$\overline{\text{OUTPUT}}$, on the schematic) are handled from the TOMIKONN pulse program. An auxiliary input for shimming is also included.

We present results from a 2D imaging obtained in situ from 200 projections in Φ, the total experience time is 12 s.

Yours sincerely,

A. BRIGUET, Y. CREMILLIEUX, A. DEGUIN, D. GRAVERON



Schematic of the unit (each channel)

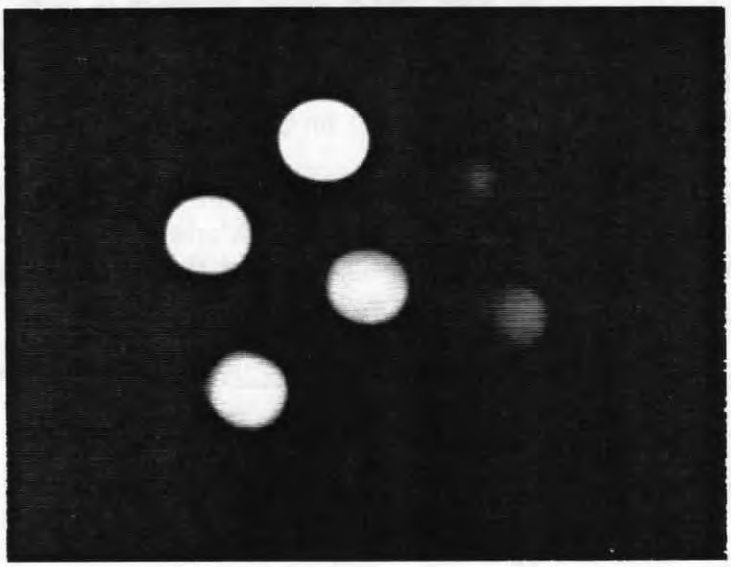


Image 2D of 7 tubes with 50 ms < T1 < 2 s
200 projections
12s total experience time

HMRI

HUNTINGTON MEDICAL RESEARCH INSTITUTES

January 18, 1993
(received 1/22/93)

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

Dear Dr. Shapiro:

Title: Well-localized, Standardized, Quantitized Short TE ^{1}H MRS Permits New Diagnostic Accuracy in Patients with Alzheimer Disease

We are well aware that clinical spectroscopy is a poor-relation of high resolution NMR in the precision and reproducibility it can offer. Nevertheless, we are confident that emphasis on standardization and quantitation can come some way to improving this imbalance.

At HMRI, we have developed a rigorous method of localized ^{1}H MRS of human brain in which peak ratio variation from day to day, and between individuals, is less than 5-7%.[1] When quantitation is added to this procedure (using an external standard and T_2 water corrections for brain compartmentation and CSF volume correcting[2]), reproducibility is less good but still close to ±10% under controlled conditions. Finally, we have followed the chemists ideal (and the approach of J. Frahm and others) in using relatively short TE (30 ms) to increase the number of resonances which can be reliably identified in the brain spectrum. Now, in a clinical setting, this extra effort is beginning to pay off. The brain in Alzheimer disease remains an enigma; the clinical precision of diagnosis may be as low as 60%, and is at best 80 +%, and the mechanism of dementia is unknown.

Using the procedures outlined above, we have identified a new marker for Alzheimer disease (AD) (elevated *myo*-inositol; Figure, bottom spectrum), which, taken in conjunction with the repeatedly observed, but non-specific loss of the putative neuronal marker (N-acetylaspartate) may lead us to a reliable diagnostic test for patients with AD.[3]

The exciting new point for the biological chemist is that regulation of cerebral *myo*-inositol, rather than modulation of choline[4] may be the desired target for innovative therapies.

1. Kreis R, Ross BD, Farrow NA and Ackerman Z. Metabolic disorders of the brain in chronic hepatic encephalopathy detected with ^{1}H MRS. *Radiology* 1992; 182:19-27.
2. Ernst T, Kreis R and Ross BD. Absolute quantitation of water and metabolites in the human brain: I. Compartments and water. *J Magn Reson* 1993; in press.

   Kreis R, Ernst T and Ross BD. Absolute quantitation of water and metabolites in the human brain: II. Metabolite concentrations. *J Magn Reson* 1993; in press.
3. Miller BL, Moats R, Shonk T, Ernst T, Wooley S and Ross BD. Proton MRS shows increased cerebral *myo*-inositol in patients with Alzheimer disease. *Radiology* 1993; in press.
4. Nitsch RM, Blusztajn JK, Pittas AG, Slack BE, Growdon JH, and Wurtman RJ. Evidence for a membrane defect in Alzheimer disease brain. *Proc Natl Acad Sci USA* 1992; 89:1671-1675.

MAGNETIC RESONANCE SPECTROSCOPY LABORATORY
660 S Fair Oaks Avenue, Pasadena, CA 91105 Phone: (818) 397-3271 Fax: (818) 397-3332

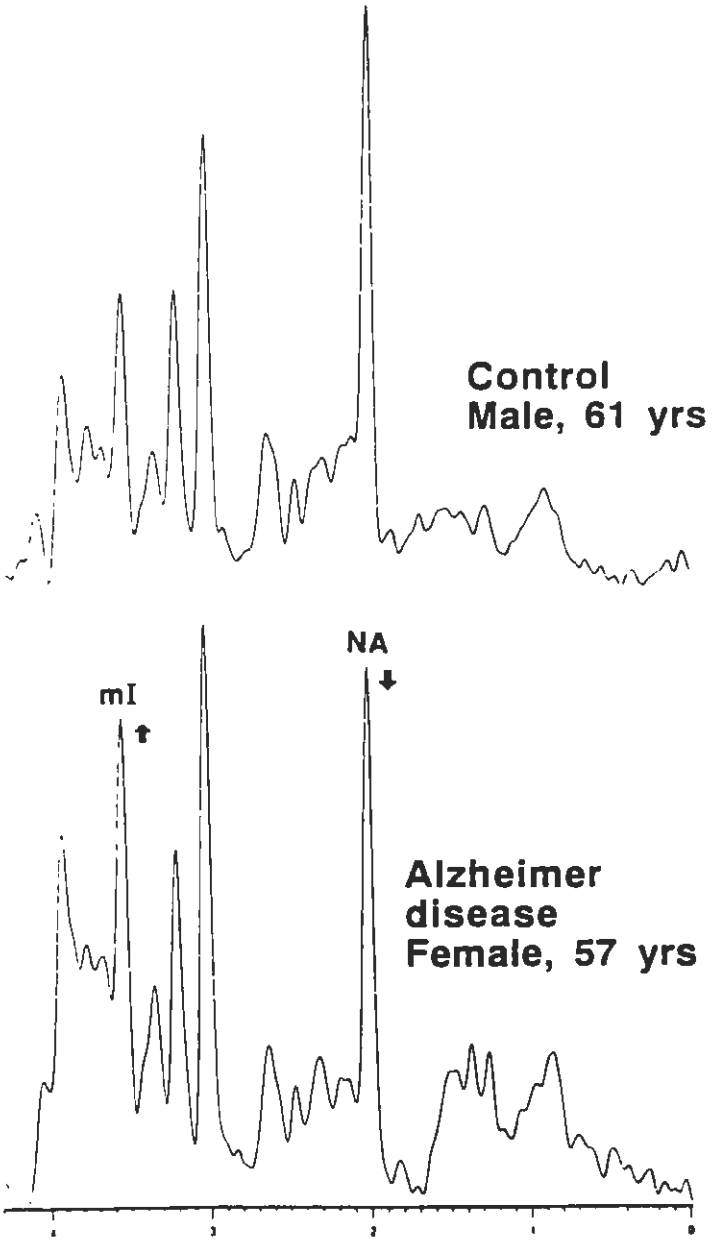


Figure: Examples of spectra from a single patient and a normal age-matched control are shown. Peak intensities are expressed relative to Cr.

Brian D. Ross, M.D., Ph.D.
Director, MRS Unit, HMRI
Visiting Associate, Caltech

Thomas Ernst, Ph.D.
University of Freiburg
Germany

Rex Moats, Ph.D.
Huntington Med. Res. Insts.

Roland Kreis, Ph.D.
University and Inselspital, Bern, Switzerland

Thanks to Dr. Bruce Miller of Harbor UCLA Medical Center for referring the patient to us, and to the L.K. Whittier Foundation for their support.

Please credit this contribution to the subscription of John D. Roberts

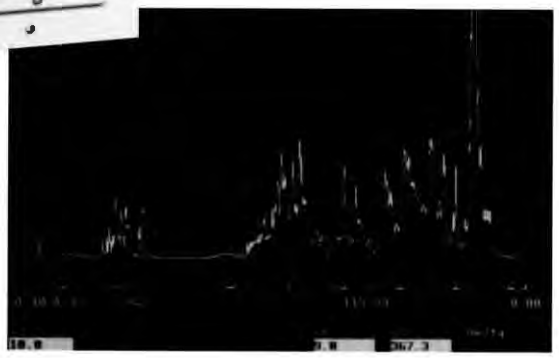
AMT Delivers More For Less!

10–90 MHz, 1000 Watt RF power amplifiers for less than $10,000

Key Features:

- Full 10–90 MHz frequency range
- 1000 watt power rating
- Linearity ±1 dB
- Noise blanking in less than 2 μs
- Less than 5% pulse droop
- Dual mode, Pulse/CW operation
- Digital power meter
- Dual range power limits

Model 3426



The AMT NMR/NMRI product family

SERIES	FREQUENCY	POWER RATINGS
3130	200–500 MHz	50 to 300 W
3200	6–220 MHz	150 to 1000 W
3304	30–310 MHz	400 W
3420	10–90 MHz	1000 to 2000 W

Call Jim Lukes at AMT, or your local distributor NOW for a price that will flip your spins!

AMERICAN MICROWAVE TECHNOLOGY

3080 Enterprise Street ■ Brea, CA 92621 ■ (714) 993-0802 ■ Fax (714) 993-1619

AMERICAN MICROWAVE TECHNOLOGY

Model 3426

10–90 MHz, pulsed, solid-state, RF power amplifier system

Electrical specifications:

Frequency range	10–90 MHz
Pulse power (min.) into 50 ohms	1000 W
CW power (max.) into 50 ohms	100 W
Linearity (± 1 dB)	0–900 W
Gain (typ.)	65 dB
Gain flatness	± 2 dB
Input/Output impedance	50 ohms
Input VSWR	< 2:1
Pulse width	20 ms
Duty cycle	Up to 10%
Amplitude rise/fall time	250 ns typ.
Amplitude droop	5% to 20 ms typ.
Phase change/output power	10° to rated power, typ.
Phase error overpulse	4° to 20 ms duration, typ.
Noise figure	11 dB typ.
Output noise (blanked)	< 20 dB over thermal
Blanking delay	< 2 μs on/off, TTL signal
Protection	1. VSWR: infinite VSWR 2. Input overdrive: up to 10 dB 3. Over duty cycle/pulse width 4. Over temperature

Supplemental characteristics:

Connectors, rear panel	1. RF input: BNC (F) 2. RF output: Type N (F) 3. Noise blanking: BNC (F) 4. Interface: 25 pin D(F), EMI filtered
Indicators, front panel	1. AC power on 2. Peak power meter 3. Over pulse width 4. Over duty cycle 5. Over temperature 6. Over drive 7. CW mode
System monitors	1. Forward/Reflected RF power 2. Over pulse width/duty cycle 3. DC power supply fault 4. Thermal fault
Front panel controls	1. AC power 2. Pulse width 3. Duty cycle
Cooling	Internal forced air
Operating temperature	+10 to 40°C
AC line voltage	208/230 VAC, ± 10%, 50–60 Hz
AC power requirements	2000 watts
Package	Rack mount
Size (HWD, inches)	8.75 × 19 × 20.25
Net weight	100 lbs.

03/92

3080 Enterprise Street ■ Brea, CA 92621 ■ (714) 993-0802 ■ Fax (714) 993-1619

PENNSTATE

College of Medicine • University Hospital
The Milton S. Hershey Medical Center

Department of Radiology

P.O. Box 850
Hershey, Pennsylvania 17033
(717) 531-6069

January 20, 1993
(received 1/22/93)

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

Dear Barry:

Evaluation of B_1 Field Homogeneity Using Field Histograms and Finite Element Calculations

The field homogeneity of radio-frequency (RF) coils is an important parameter for determining the quality of an RF coil. Previous investigations have shown that Fourier transformation of the signal intensity as a function of nutation angle produces a histogram of the coil's magnetic field (B_1 field) (1, 2), which is a direct measure of the global B_1 field homogeneity. We have created the theoretical and experimental histograms of B_1 field of RF coils. The calculated histogram can be directly compared with the experimental histogram to verify the findings from the computer simulation. Several commonly used RF coils have been evaluated using both calculated and experimental histograms (3). In addition, the optimized configurations of those coils have been suggested based on the results of the calculated histograms (4).

The computer calculations were performed using Maxwell 2D Field Simulator software developed by the Ansoft Corporation at Pittisburgh, PA. The software uses finite element analysis to solve the full set of the Maxwell equations for the time-varying electromagnetic field problems. The software calculates the magnetic vector potential **A**. The magnetic induction **B** is then calculated using the equation $\mathbf{B}=\nabla\mathrm{x}\mathbf{A}$. The finite element calculation solves the numerical solution in such a way that the solution is simultaneously consistent for both the field and the current distribution. Thus, this solution will produce the field map which matches the experimental situation more realistically than other calculations. The calculated histograms were created by plotting the field population versus B_1 field magnitude, where the field population is the number of the sampling points which have the same B_1 magnitude. The field homogeneity of the birdcage coil, the slotted tube resonator, the multiple wire coil and the radial plate coil were evaluated. The coil models were assumed to be the cross section of the infinitely long cylinder coils with the inner diameter of 40 mm. Several geometrical parameters have been changed in the coil optimization. The optimum configurations of four types of RF coils are suggested. It is found that the field homogeneity is more strongly dependent on the window angle than other parameters.

A single pulse sequence is used to generate the experimental histogram of the B_1 field. The RF coils were built with the same diameter as the computer models. A series of free induction decay signals were acquired as the pulse width was incrementally increased. Seventy to one hundred spectra were collected on resonance. A curve of signal intensity vs. pulse width was obtained. Fourier transformation of this curve produces a B_1 histogram.

The experimental and calculated histograms for a radial plate coil and a multiple wire coil are shown in Fig. 1 and Fig. 2, respectively. Figure 1a and 2a are the 2D contour plots of B_1 field, 1b and 2b are the calculated histograms and 1c and 2c are the experimental histograms. The experimental histograms are found to be consistent with the calculated histograms. The histograms are more sensitive to describe field homogeneity than 2D contour plots. Details of the histogram technique are described in two manuscripts which have been submitted.

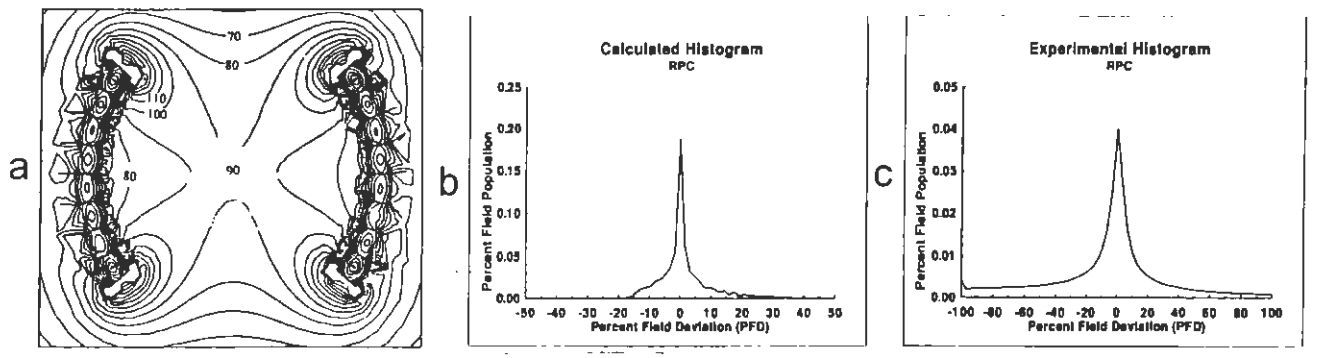


Figure 1. The contour plot and bistograms for a radial plate coil

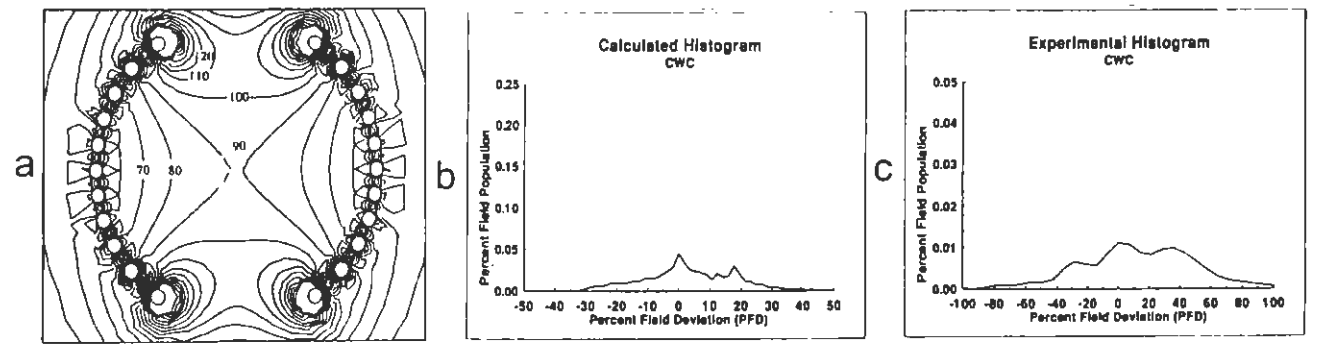


Figure 2. The contour plot and histograms for a multiple wire coil

Off-Line Processing

As self-inflicted punishment for the tardiness of this submission we would like to additionally call attention to some off-line processing for the PC. We have transferred *in vivo* serial spectra from our Aspect computer via WIN-NMR for the PC using RS232C protocol. A Winbatch program has been added to the Bruker software to allow automated transfer of the serial spectra and also converts the binary files to ASCII files. A spectral and general nonlinear curvefitting program, Peakfit (™ Jandel Scientific) inputs and automatically fits the serial data.

The automation capabilities make these inexpensive procedures convenient for off hour processing. We have also transferred and processed serial spectra from out Nicolet 1280 system.

Sincerely,

Casey S. Li
li@psuhmed

Qing X. Yang

Michael B. Smith

Gerald D. Williams*
jerry@psuhmed

(1) K. Mehr, E. Koeller, and W. Kuhn, Abstr. of 33rd ENC, 1992, p. 264.
(2) S. L. Talaga and J. Gillien, J. Magn. Reson. **94**, 493 (1991).
(3) Q. X. Yang, C. S. Li, and M. B. Smith, Abstr. 11th SMRM Meeting, 1992, p. 4307.
(4) C. S. Li, Q. X. Yang, and M. B. Smith, Abstr. 34th ENC, 1993.

* Please credit this contribution to GDW.

SENIOR NMR SPECTROSCOPIST-SENIOR MOLECULAR MODELER

Indiana University is seeking qualified candidates for the position of Senior NMR Spectroscopist-Molecular Modeler in the Department of Chemistry. The successful candidate will manage the training activities of the Departmental NMR Facility and the Departmental Molecular Modelling Facility, and collaborate in the design of new non-routine NMR and molecular modelling experiments. Candidates should have the following minimum qualifications: Ph.D. or equivalent in Chemistry or a related area plus 2 to 4 years experience in NMR and molecular modelling, and excellent communication and interpersonal skills. Demonstrated experience in daily operation of modern high resolution NMR spectrometers is required and experience with Silicon Graphics (SG-VGX and Personal Iris) systems is highly desirable. Please submit the names of three references along with your resume. Applications received by March 15 will be assured consideration. Please send your application to: Dr. John C. Huffman, Indiana University, Chemistry Department, Bloomington, IN 47405.

THE UNIVERSITY OF UTAH

Darrell R. Davis
Assistant Professor
(801) 581-7006
FAX: 581-7087
davis@adenosine.pharm.utah.edu

January 12, 1993
(received 1/16/93)

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

Felix 3D Macros.

Dear Barry:

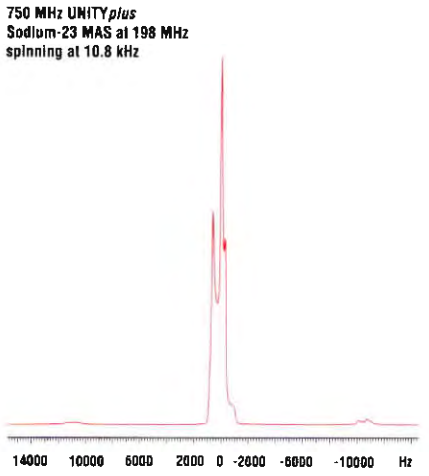
Like a lot of folks we have started to do a lot of 3D and are trying to figure out what we have. Based on some discussions with the guys at HRI we thought the readers might be interested in some of the macros we are using for processing Varian 3D data with Felix 2.1. These macros are for data that is hypercomplex in both F1 and F2. The first macro is the loading, F3 macro. The 'd1_3dft.mac' macro is to process the F1 domain and a D2 macro can be similarly constructed. For 2D processing of 3D data, 'ni2_pst2' is the loading macro, 'd1_3dft.mac' can then be used. Details like phasing and weighting have been left out to save space. We want to thank Mike Wittekind for some helpful hints in the early stages.

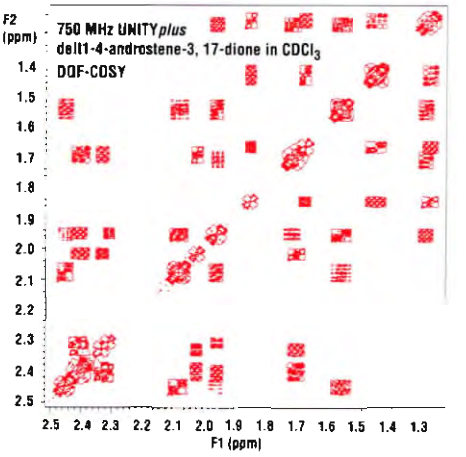
```
c**ntd3.mac
c**Hypercomplex in t1 and t2
c** Load the 3D data
c**Varian phase cycling
c**
cl
for count2 1 &ni2
ty  t2-slice#=&count2
ty
for count1 1 &ni
re &datfil
def datype 1
def datsiz 512
ft
red
eva vec1 (2*&count1-1)
eva vec2 (2*&count2-1)
sto &vec1 &vec2 0
re &datfil
def datype 1
def datsiz 512
ft
red
eva vec2 (2*&count2)
sto &vec1 &vec2 0
re &datfil
def datype 1
def datsiz 512
ft
red
eva vec1 (2*&count1)
eva vec2 (2*&count2-1)
sto &vec1 &vec2 0
re &datfil
def datype 1
def datsiz 512
ft
red
eva vec2 (2*&count2)
sto &vec1 &vec2 0
next
next
ty
end

c**ni2_pst2
c** 2D FT of 3D States data.
c** FT of the F2 F3 domain
cl
def phase0 150
def phase1 186
def pivot 50
for count1 1 &ni2
re &datfil
def datype 1
def datsiz 512
ft
red
eva vec1 (2*&count1-1)
sto &vec1  0
re &datfil
def datype 1
def datsiz 512
ft
red
eva vec1 (2*&count1)
sto &vec1  0
re &datfil
re &datfil
for count2 1 79
re &datfil
re &datfil
re &datfil
re &datfil
next
ty Increment=&count1
next
ty
end

c**d1_3dft.mac
c**NOE-NOE D1 3D FT
c**
bun 1
for vec1 1 &vector
lwb &vec1
def datype 1
cnj
def datsiz 80
lpl 80 16 8 81 128
qsb 128 90 .9
zf 256
ft
ph
red
swb &vec1
ty  vector=&vec1 $
next
bun 0
end
```

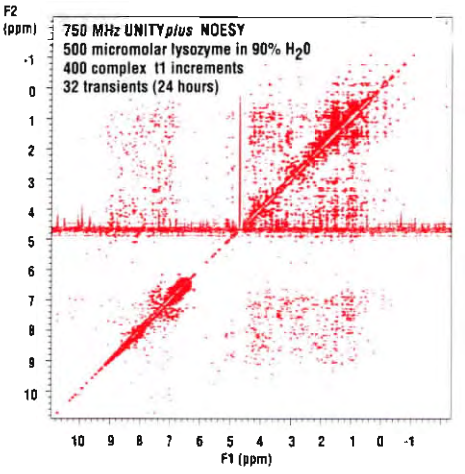
Department of Medicinal Chemistry

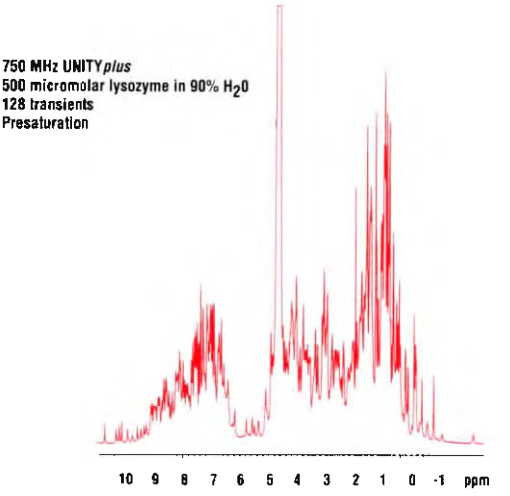
308 Skaggs Hall
Salt Lake City, Utah 84112
(801) 581-7063 FAX (801) 581-7087

Varian Delivers 750 MHz Results.









These spectra were obtained on a Varian 750 MHz UNITYplus™ NMR spectrometer.

Leadership in NMR Technology

Varian Associates, Inc. and Oxford Instruments have jointly developed the first 750 MHz NMR system.

Ideal for biomolecular and chemical applications, Varian UNITY*plus* NMR spectrometers perform the most demanding experiments at all field strengths. Oxford 750 MHz magnets provide the best long-term stability and do not require cryo-pumping. Uniquely designed as a single, no-compromise platform for liquids, solids, and microimaging at the widest range of field strengths, the UNITY*plus* offers the most advanced technology to the NMR community. Varian's exceptional probes, pulsed field gradients, and flexible software provide the ideal system for leading-edge NMR research.

For additional information, contact the Varian office nearest you.

Varian Associates 3120 Hansen Way, Bldg. 4, Palo Alto, CA 94304-1030, U.S.A. Tel. 1-800-356-4437 • **Varian International AG** Kollerstrasse 38, CH-6303, Zug, Switzerland Tel: (42) 44 88 44 • **Varian GmbH** Alsfelderstrasse 6, D-6100 Darmstadt, Germany Tel: (0 61 51) 70 30 • **Varian Instruments Ltd.** 3rd Matsuda Bldg., 2-2-6 Ohkubo-Shinjuku, Tokyo, Japan Tel. (3) 3204-1211

varian

Varian's 750 MHz Spectrometers Provide Results

Advantages

- Highest chemical shift dispersion and sensitivity in a persistent, non-pumped magnet
- Outstanding performance and stability is delivered by the UNITY*plus* NMR system
- Greatest flexibility is provided by VNMR software

Applications

- Structure determination of biomolecules
- Detection of minute sample quantities
- MAS studies of quadrupolar nuclei
- Methods development at high field strengths

Call your sales representative. Australia (3) 543 8022. Austria (1) 69 55 450. Belgium (2) 721 4850. Brazil (11) 829 5444. Canada (416) 457 4130. Denmark (42) 84 6166. France (1) 69 86 38 38. Germany (6151) 70 30. Italy (2) 753 1651. Japan (3) 3204 2111. Korea (2) 561 1626. Mexico (5) 533 5985. Netherlands (3403) 50909. Norway (9) 86 74 70. Spain (01) 430 0414. Sweden (8) 52 00 30. Switzerland (42) 44 88 44. UK (932) 24 37 41. US 800-356-4437. Other International (415)424-5424

MAG-6055/569

varian

1842

Faculty of Chemical Technology and Materials Science
Delft University of Technology

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

(received 1/14/93)

S. Jahromi
Technical University Delft
ST (TMS)
Julianalaan 136
2628 BL Delft
Tel: 015-782626

Copolymerization of liquid crystalline di-epoxides with aromatic di-amines; Monitoring the reaction with **Real Time ^{2}H-NMR**

Dear Prof. Shapiro,

Ordered polymeric networks are becoming increasingly the topic of current research in the field of liquid crystalline poymers, due to their excellent anisotropic optical and mechanical properties. The basic idea in the production of highly ordered and highly crosslinked networks is to orientate uniaxially low molecular weight liquid crystalline monomers and subsequently freeze in the orientation by polymerization. The polymerizing units we have chosen, are di-epoxide monomers which are copolymerized (i.e. cured) with aromatic amines. Scientifically it is of special interest to monitor in situ, the changes in properties (e.g. degree of order) during the network formation.

As you might very well know a powerfull technique for studying liquid crystalline materials is ^{2}H-NMR[1]. By deuterating selectively each of the two reacting monomers we have been able to monitor the polymerization in real time at elevated temperatures. By adjusting the spectrometer settings and the amount of deuterated compounds, it was possible to measure a very well resolved spectrum within one minute. This is quite favourable considering the totale reaction time is two hrs. The observed quadrupolar splittings were as expected, very sensitive to changes in molecular weight and average orientation of the medium. Furthermore, valuable information could be obtained concerning the local structure and network formation[2].

Sincerely,
S. Jahromi

S. Jahromi

1) Emsley, J,W., "Nuclear Magnetic Resonance of Liquid Crystals", Reidel, Dordrecht, 1985
2) Jahromi, S., to be published.

Please credit this contribution to Dr. J.A. Peters's subscription.

413-24

NORTHWESTERN UNIVERSITY

Joseph B. Lambert
Clare Hamilton Hall Professor of Chemistry

Department of Chemistry
2145 Sheridan Road
Evanston, Illinois 60208-3113
Telephone (708) 491-5437
Internet lambert@casbah.acns.nwu.edu
Facsimile (708) 491-7713

December 23, 1992
(received 12/26/92)

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

Dear Barry:

Last year we wrote you about unusually low field tin-119 chemical shifts associated with low valent tin species, formulated as R_3Sn^+. We have now been able to extend those observations to silicon through the use of a very stable new anion for these systems, tetrakis(pentafluorophenyl)borate or $B(C_6F_5)_4^-$. We react the trityl salt, $(C_6H_5)_3C^+$, of this anion in a low coordinating solvent such as benzene with a hydridosilane such as triethylsilane, Et_3SiH. The formal products are Et_3Si^+ as the borate salt and triphenylmethane. Evaporation of the solvent followed by washing with hexane removes triphenylmethane and leaves a solid that can be examined directly by solid state ^{29}Si NMR methods or can be dissolved in any number of solvents for solution spectroscopy. The following table gives a few of the results we have obtained.

Silicon-29 Chemical Shifts for R_3Si^+ $B(C_6F_5)_4^-$

R	Solvent	δ from TMS	δ from R_3SiH (same R)
Me	C_6D_6	83.6	101.1
Et	none (solid)	94.3	94.1
	C_6D_6	92.3	92.1
	toluene	81.8	81.5
	sulfolane	58.4	58.1
	CH_3CN	36.7	30.7
iPr	C_6D_6	107.5	95.5
Me_3Si	C_6D_6	111.1	228.5

The result for the silyl substituent, some 228 ppm downfield from the silane, is consistent with an essentially free silyl cation. The shifts for the alkyl substituents in the solid or in hydrocarbon solvents are around 100 ppm and suggest either an agostic interaction or some complexation with solvent or anion. As the complexing ability of the solvent increases, the chemical shift moves upfield, indicating that complexation with solvent is variable. Finally complexation with the anion is very loose, as the boron-11 chemical shift and linewidth are identical to those of trityl borate. Moreover, the fluorine-19 chemical shifts are identical in the silyl and trityl salts.

Sincerely,

Joseph B. Lambert

Shizhong Zhang

Lehigh University

Department of Chemistry
telephone (215) 758-3470
fax (215) 758-3461

Seeley G. Mudd Building
Lehigh University
6. East Packer Avenue
Bethlehem, PA 18015-3172

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

January 6, 1993
(received 1/14/93)

NMR Studies of β-cyclodextrin:Porphyrin Complexes

Dear Dr. Shapiro:

We are currently evaluating the interactions of meso-substituted porphyrins with β-cyclodextrin (βCD) by NMR as the initial step in a larger study of porphyrin-carbohydrate interactions. Changes in the chemical shift of protons on both the βCD and porphyrin can be monitored, and by applying the method of continuous variations, using Job's plots, these changes can be used to determine the stoichiometry of the βCD:porphyrin inclusion complexes formed.

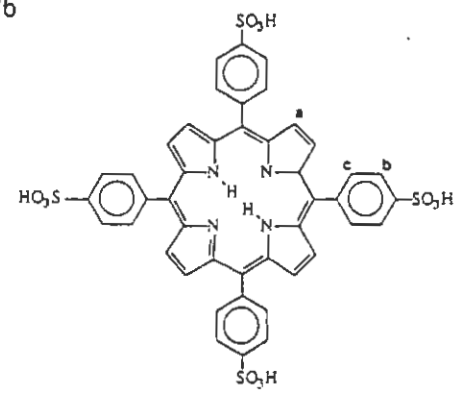
Aqueous solutions of βCD and tetra-4-sulfonatophenyl porphyrin ($TPPS_4$) have been studied. The total concentration of all solutions (3.64 mM) was constant for all measurements, and the mole fractions of βCD and porphyrin were varied between 0.1 and 0.9. The following figures show the Job's plots derived from changes in chemical shift of protons as a function of mole fraction of species present. From the maxima at 0.8 in the βCD plot and 0.2 in the porphyrin plot, one may infer the presence of a complex with the stoichiometry 1 porphyrin : 4 βCD.

Typically the guest molecules included in a βCD cavity contain a phenyl ring, whose presence in the βCD causes changes in the chemical shift of the proton inside the cavity (proton 3 on graph 2) because of its shielding cone. We have observed that the chemical shifts of protons on the outside of the βCD (protons 2 and 4 on graph 2) are also effected by association with a meso-substituted porphyrin. We suggest that these shifts are due to the location of the βCD in the shielding cone of the porphyrin ring and may potentially be useful in describing not only the stoichiometry but also the structure of the complex.

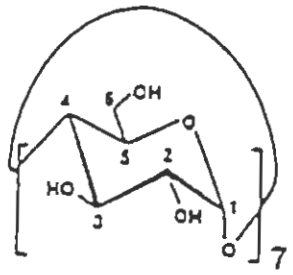
Results of similar experiments with other meso-substituted phenyl porphyrins and βCD indicate the presence of complexes with different stoichiometries. Because certain key proton peaks are unresolved or poorly resolved in these complexes, we are now using 2D NMR techniques to identify these proton signals unambiguously and to measure their chemical shifts. Additional quantitative evaluations of the effect of the shielding cone of the porphyrin on chemical shift are underway to elucidate the architecture of the complexes.

Sincerely,

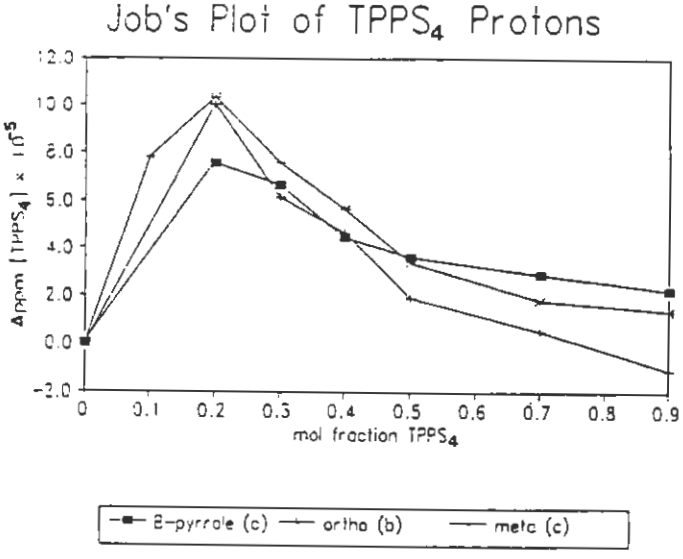
Andrew N. Brimer Natalie Foster William R. Anderson, Jr

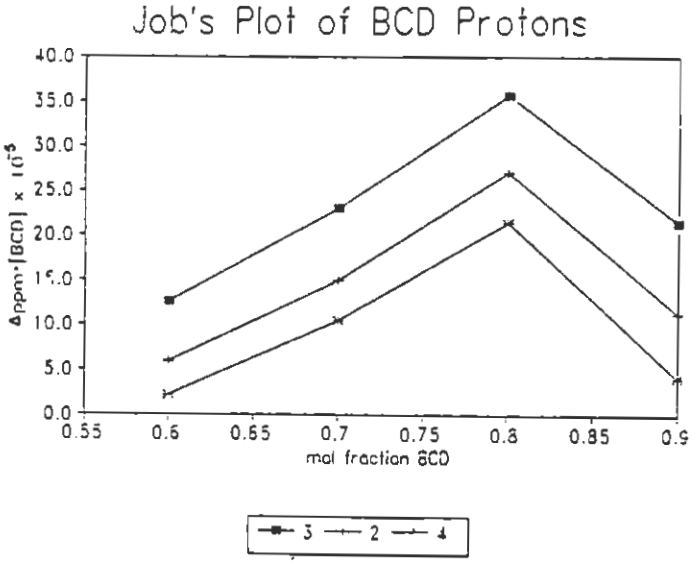


tetra-sulfonatophenyl porphyrin



β-cyclodextrin





<u>Postdoctoral Position Available in Chemistry Department, National Tsing Hua University, Hsinchu, Taiwan</u>

Postdoctoral positions are now available. Persons with a strong interest and background in the following fields:

1. Protein engineering
2. Multi-dimensional NMR on proteins/peptides
3. Molecular modeling/dynamics/mechanics

Salary is approximately $20,000 U.S. dollar per year (commensurate with background and experience). Our laboratory is equipped with AM-400, Unity-400, Gemini-300 and MSL-200 NMR spectrometers. A 600 MHz NMR instrument will be installed this year. Workstations (IRIS 4D/35, INDIGO, IBM R600/280, μVax III) and softwares (QUANTA, CHAEMM, X-PLOR, INSIGHT II, DISCOVER, DIANA, FELIX) are dedicated for 3D structural determination of proteins/peptides.

Interested applications should send a resume to Professor Chin Yu, Chemistry Department, National Tsing Hua University, Hsinchu, Taiwan.

Structure Elucidation

CSEARCH

Offers identical presentation on Sun, Silicon Graphics, or VMS

Reads ^{13}C NMR peak tables directly

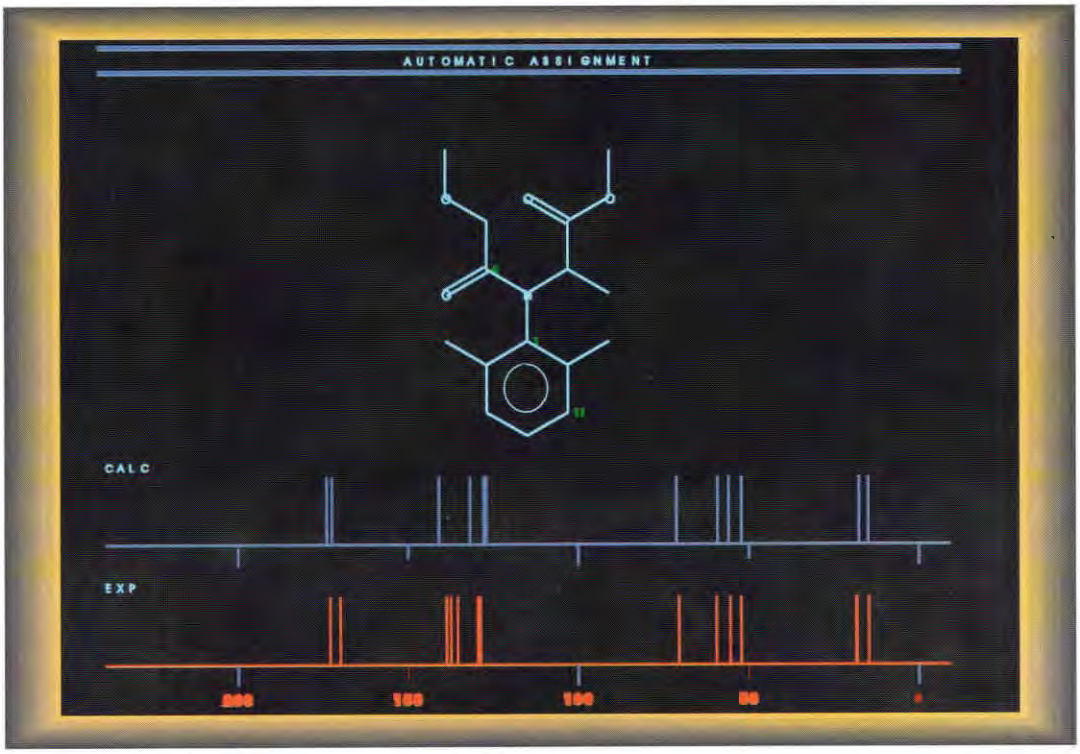
Confirms calculated with measured spectrum

Finds structurally related compounds by spectral matching

Calculates spectra for compounds not in the database

Sun is a trademark of Sun Microsystems, Inc. VMS is a trademark of Digital Equipment Corporation. Silicon Graphics is a trademark of Silicon Graphics, Inc.

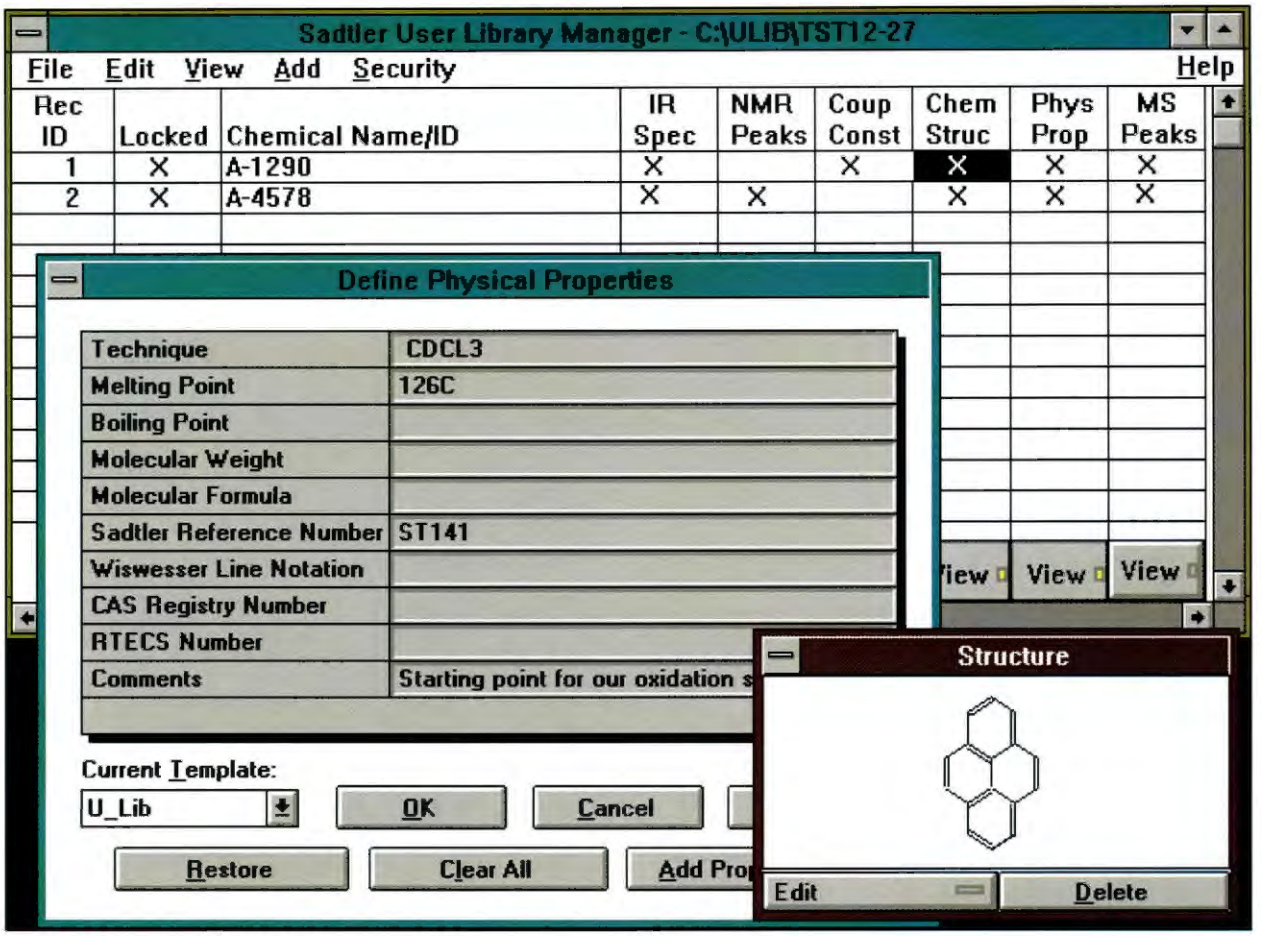
Comparison of the calculated spectrum of a proposed structure with its measured spectrum. The intelligence of CSEARCH is demonstrated by favorable comparison for a structure not contained within the database of 52,000 spectra.



BIO-RAD **Sadtler Division**

Main Office, *3316 Spring Garden Street, Philadelphia, Pennsylvania 19104. Telephone: (215) 382-7800. Telefax: (215) 662-0585. TWX: 710 670-1186.*

Those with the BEST INFORMATION WIN



Software and Databases for Personal Computers

BIO-RAD **Sadtler Division**

Main Office, 3316 Spring Garden Street, Philadelphia, Pennsylvania 19104.
Telephone: (215) 382-7800. Telefax: (215) 662-0585. TWX: 710 670-1186.

THE UPJOHN COMPANY
301 Henrietta Street
Kalamazoo, MI 49001-0199

UPJOHN LABORATORIES
Brian J. Stockman Ph.D.
Research Scientist
Physical & Analytical Chemistry
7255-209-007
Tel (616) 385-7582
Fax (616) 385-7522

December 18, 1992 (received 12/22/92)

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

Dear Dr. Shapiro:

Secondary structure dependent chemical shifts in proteins, recognized almost ten years ago (1,2), have come under increasing scrutiny lately (3,4). This has occurred for two main reasons. First, larger and larger data bases correlating secondary chemical shifts with locations of secondary structure have been developed (3), and second, non-NOE-based assignment strategies require supplementary data to substantiate regions of secondary structure (4). Our interest in secondary structure dependent chemical shifts has been in the comparison of the locations of secondary structure in highly homologous proteins.

In order to expedite this process, we have developed a Microsoft Excel spreadsheet that calculates the secondary chemical shift values automatically. For each residue, the user enters the residue type, sequence number, and observed chemical shifts for proton, carbon, and/or nitrogen resonances. The spreadsheet, by reference to cells containing the random coil chemical shifts for each residue type, calculates the secondary shifts in a separate column of cells. Using the graphing capabilities of Excel, the secondary chemical shifts are easily plotted against sequence number.

As an example, we have been investigating the solution structure of the flavodoxin from *Desulfovibrio vulgaris*. The flavodoxin from this species is 21 residues shorter than that from *Anacystis nidulans*. Complete main-chain chemical shifts for the *D. vulgaris* (5) and *A. nidulans* (6) flavodoxins were entered into the spreadsheet as described above. A plot comparing the secondary $^1H^\alpha$ chemical shifts is shown in Figure 1. Positive secondary chemical shifts correspond to residues in β-sheet (labeled βI, βII...), while negative secondary chemical shifts correspond to α-helical residues (labeled αI, αII...). It is apparent from the two plots that while strand I of the β-sheet in both proteins is located at the same position in the primary sequence, strands II, III, and IV are offset by several residues. This results from five deletions between residues 25-60 in the *A. nidulans* primary sequence based on alignment with the *D. vulgaris* primary sequence. More striking, however, is the large offset in the location of the fourth α-helix. This offset is caused by a 20-residue insertion near position 120 in the *A. nidulans* sequence. The differences in locations of secondary structure elements as defined here are identical to those observed in the X-ray crystal structures of the two proteins.

Our spreadsheet has been developed for Excel running on Macintosh systems, and is easily adapted to any primary sequence. Copies of the template file we have used are available on request. A brief description of how to enter and use the data will also be provided.

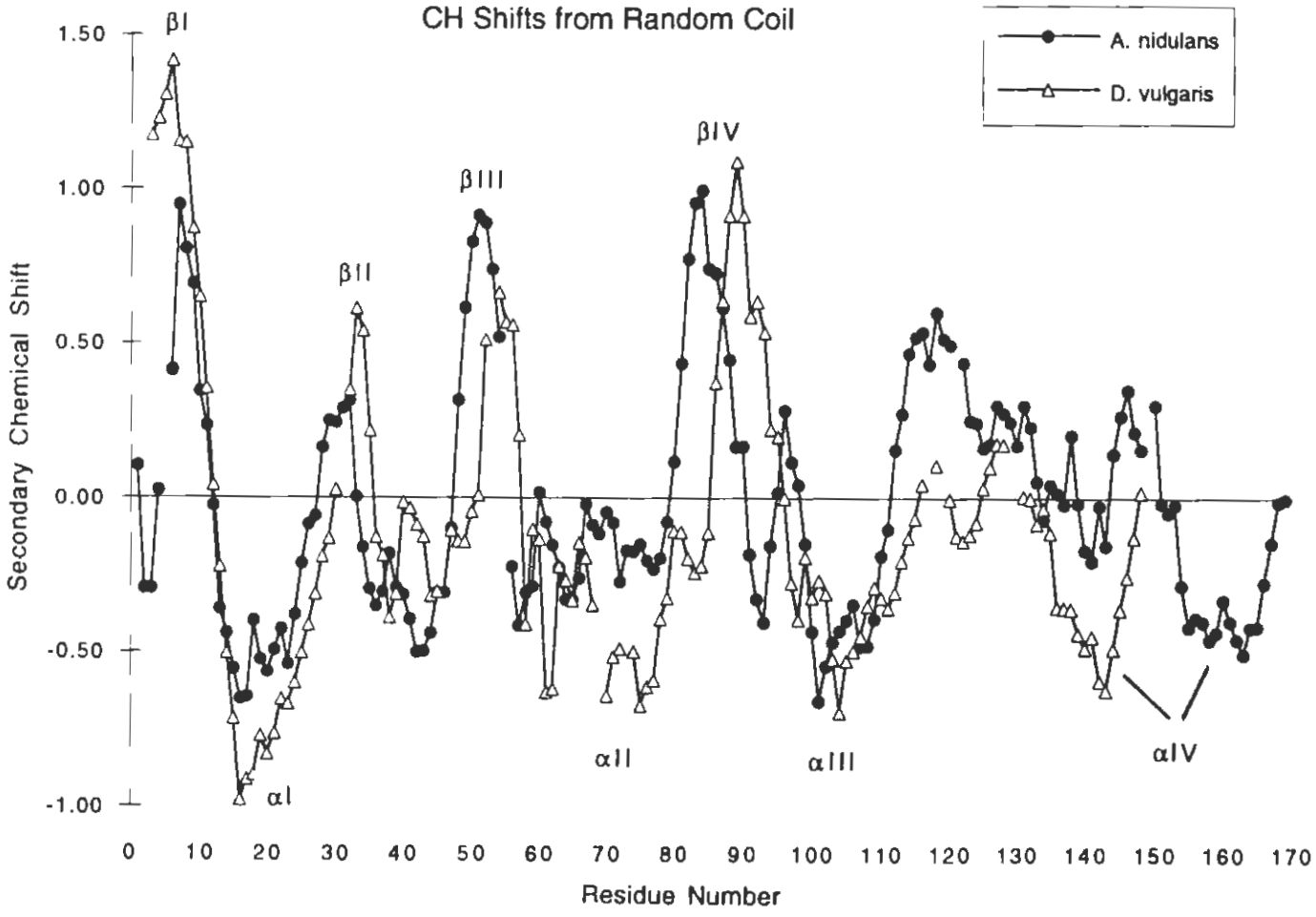


Figure 1. Comparison of secondary $^1H^\alpha$ chemical shifts for two flavodoxins.

1. Dalgarno, D. C., Levine, B. A., & Williams, R. J. P. (1983) *Bioscience Rep. 3*, 443-452.
2. Pardi, A., Wagner, G., & Wüthrich, K. (1983) *Eur. J. Bioch. 137*, 445-454.
3. Wishart, D. S., Sykes, B. D., & Richards, F. M. (1991) *J. Mol. Biol. 222*, 311-333.
4. Wishart, D. S., Sykes, B. D., & Richards, F. M. (1991) *Biochemistry 31*, 1647-1651.
5. Stockman, B. J., Euvrard, A., Kloosterman, D. A., Scahill, T. A., & Swenson, R. P. (1993) *J. Biomol. NMR*, in press.
6. Clubb, R. T., Thanabal, V., Osborne, C., & Wagner, G. (1991) *Biochemistry 30*, 7718-7730.

Sincerely,

Brian J. Stockman Terrence A. Scahill

Please credit this contribution to the account of Dr. Paul Fagerness.

Position Available

I currently have an opening for a postdoctoral scientist in my lab in the Physical and Analytical Chemistry unit of The Upjohn Company. The position will involve the application of multi-dimensional NMR spectroscopy to isotopically enriched proteins and protein-ligand complexes. The appointment is for a period of one year, renewable for a second and possibly a third year.

The successful candidate will collaborate with scientists in the computational chemistry, biochemistry, molecular biology, and adhesion biology units of Upjohn. Applicants should have a recent or soon to be received Ph.D. in Chemistry, Biochemistry, or a related field, with experience in the application of NMR methods to investigate protein structure or protein-ligand interactions.

Our state-of-the-art facilities include fully equipped Bruker AMX600, AMX500 and ARX400 spectrometers for data collection and Silicon Graphics workstations for data processing (FELIX, NMRZ) and structure calculation and refinement (DGII).

For further information, please contact Dr. Brian J. Stockman, The Upjohn Co., MS 7255-209-0, 301 Henrietta St., Kalamazoo, MI 49001. Telephone (616) 385-7582.

Thomas L. James, Ph.D.
UCSF Magnetic Resonance Laboratory
Department of Pharmaceutical Chemistry
The University of California
926 Medical Science
San Francisco, CA 94143-0446
(415) 476-1569
FAX NUMBER: (415) 476-0688

University of California, San Francisco ... A Health Science Campus **UCSF**

December 29, 1992

Re: Horizontal Bore Magnet and Spectroscopy/Imaging Console for Sale

Dear Barry:

Among other NMR systems, we own two Nalorac spectroscopy/imaging consoles with horizontal bore magnets. Although they are both in excellent working condition, space problems at UCSF, with quite possibly the highest tesla/ft^2 density of any NMR lab on earth, necessitate that we sell one. Consequently, we wish to sell either whole (preferably) or in part a console from Nalorac Cryogenics Corp. (upgraded in 1991) with a Nalorac magnet (5.6T, 4 inch clear bore), shim and gradient coils. A list of available amplifiers, RF modules, power supplies (including nearly new Techron 7550 gradient power supply), probes, disks, and other affiliated hardware and software can be obtained from Dr. Lee-Hong Chang at 415-476-8098 (phone), 415-476-0688 (fax) or chang@picasso.mmwb.ucsf.edu (e-mail).

HAPPY NEW YEAR!!!

Sincerely yours,

Tom

Thomas L. James Lee-Hong Chang

TLJ:sun

413-32

PSC OFFERS NUCLEAR MAGNETIC RESONANCE DATA WORKSHOP
July 6-9, 1993

Pittsburgh Supercomputing Center (PSC) is offering biomedical researchers an applications workshop on Nuclear Magnetic Resonance (NMR) data. The objective of this workshop is to introduce participants to different techniques for the elucidation of solution structures of proteins and nucleic acids from NMR interproton distance constraints. Topics to be covered include data reduction, simulated annealing, distance geometry, back calculations and refinements.

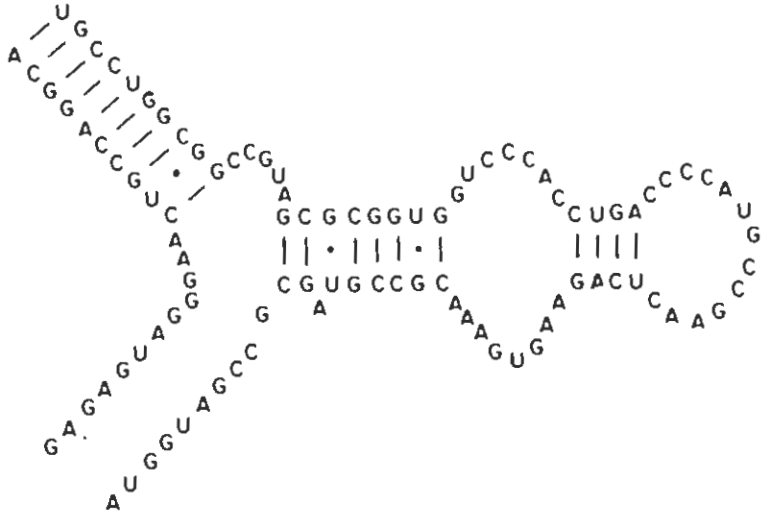
Workshop leaders are: Dr. Axel Brunger, Yale University; Dr. Thomas James, University of California, San Francisco; and Dr. Michael Nilges, European Molecular Biology Laboratory, Heidelberg. Hands-on sessions will be emphasized and participants are encouraged to bring relevant problems from their current research. No prior supercomputing experience is necessary.

This workshop is funded by a grant from the Biomedical Research Technology Program, National Center for Research Resources, National Institutes of Health. Travel, meals and hotel accommodations for academic participants are supported by this grant. Enrollment is limited to 20. **Deadline for applications is: May 14, 1993.**

For further information, contact: Nancy Blankenstein, Pittsburgh Supercomputing Center, 4400 Fifth Avenue, Pittsburgh, PA 15213; (412) 268-4960; internet: blankens@psc.edu; bitnet: blankens@cpwpsca.

Whodunnit? - A Contest.

Guess the identity of the creator of the whatever which appears below, and win a prize (not a *big* prize).



Floor plan of the cysteine chapel

CMX Multi-Channel Applications

The unique channel modularity design of the Chemagnetics™ CMX spectrometer gives you the NMR flexibility you need for solids, liquids and microimaging. The CMX offers the range of capabilities required for today's wide variety of experiments by supporting multiple channels. And the CMX design allows new channels to be added easily and affordably. All this adds up to a "no-compromise" approach to experimental capability.

Chemagnetics utilizes the latest technology to put multi-channel flexibility in the hands of the spectroscopist. Dual 16 bit, 1 MHz digitizers offer maximum dynamic range over the widest bandwidths. And each RF channel in the CMX is equipped with its own pulse programmer, so experiments are never limited by pulse programmer capacity.

The CMX is designed to start small *and* grow, providing the whole spectrum of NMR capabilities as they evolve, when you need them. Multi-channel capability with the CMX - flexibility for tomorrow, available today from Chemagnetics.

One Channel

Solids	Liquids
▪ MAS	▪ NOESY
▪ DOR	▪ TOCSY
▪ Wideline	▪ COSY
▪ CRAMPS	▪ Proton/Fluorine

Two Channels

Imaging	Solids	Liquids	Liquids+Imaging
	▪ Rotational Resonance ▪ CP/MAS ▪ HETCOR	▪ HCCH-TOCSY ▪ Reverse Detection ▪ HETCOR ▪ X-Decoupled	▪ ^{1}H, ^{19}F, Gradient Field Spectroscopy

Three Channels

Solids	Liquids	Liquids+Imaging
▪ REDOR	▪ Triple Resonance ▪ ^{1}H, ^{13}C, ^{15}N, HMQC-TOCSY	▪ H/X Gradient Field Spectroscopy

Four Channels

Liquids	Liquids+Imaging
▪ Advanced 4-channel Solution State	▪ Multi-Channel Gradient Field Spectroscopy

Chemagnetics

Dedicated to Design Excellence

Corporate Headquarters
Chemagnetics, Inc.
2555 Midpoint Drive
Fort Collins, Colorado 80525
303–484–0428
1–800–4 OTSUKA
Fax 303–484–0487

Europe - U.K.
Otsuka Electronics Europe, Ltd.
Claro Court Business Centre
Claro Road
Harrogate, HGI 4BA
United Kingdom
Phone 0423 531 645
Fax 0423 531 647

Europe - France
Otsuka Electronics Europe, SARL
"Le Copernic"
Park d'Innovation
67400 Strasbourg–Illkirch, France
Phone 088 66 82 00
Fax 088 66 82 04

Japan
Otsuka Electronics Co., Ltd.
2F Hashikan-LK Building
1–6, Azuma-Cho
Hachioji, Tokyo 192
Japan
Phone 0426–44–4951
Fax 0426–44–4961

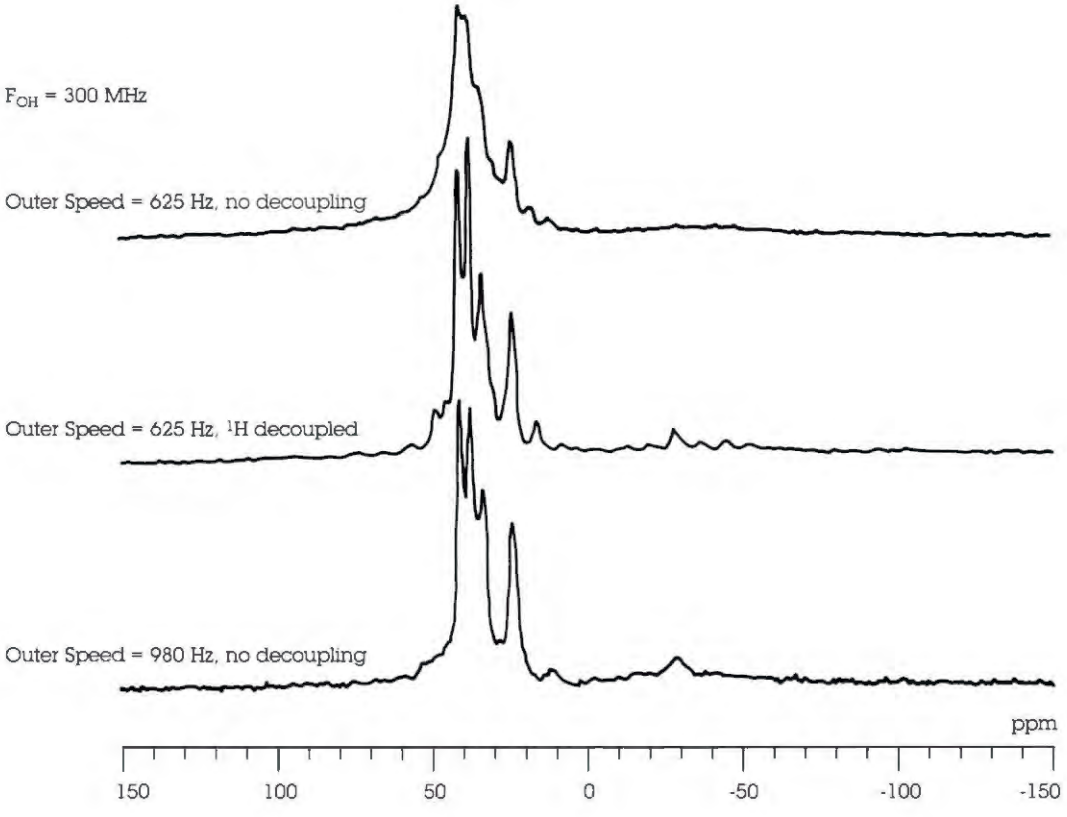
Leading the Way in Double Rotation

Double Resonance DOR from Chemagnetics

Double rotation has revolutionized the study of quadrupolar nuclei by providing structural information previously hidden by 2nd order quadrupolar broadening. When applied with proton decoupling, broadening from proton dipolar coupling is eliminated, and resolution is greatly improved. Cross polarization also enhances the signal from strongly coupled octahedral hydrated sites compared with weakly coupled tetrahedral sites.

These spectra of AlPO-11 below illustrate these effects. The top spectrum shows single resonance DOR at 625 Hz spinning. The bottom trace shows significant improvement at 980 Hz; note especially the appearance of the octahedral peak at 30 ppm. The middle trace shows 625 Hz DOR with proton decoupling; the peaks are narrower than at 980 Hz, especially the octahedral signal.

The Double Resonance DOR probe from Chemagnetics™ is available today to help you achieve the best possible resolution of chemical shifts. Call now for our latest application note on this exciting new technique.



Chemagnetics

Department of Chemistry
University of Helsinki
Finland

December 14, 1992
(received 12/19/92)

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

1992 Nuclear Quadrupole Moments

Dear Professor Shapiro,

I have recently updated the IUPAC "Quantities, Units and Symbols in Physical Chemistry", 2nd Ed., Blackwells, Oxford (1992), as far as nuclear quadrupole moments are concerned. The background for the 20 first elements is described in ref. [2]. The very latest values are listed in the four-page report [1]. Most values for the heavier elements are taken from [3].

Copies of [1] can be obtained from us (Department of Chemistry, P.O.Box 19 (Et. Hesperiankatu 4), 00014 University of Helsinki, Finland). FAX 358-0-406 159, Tel. 358-0-191 7242, Bitnet PYYKKO at FINUHA. Internet PYYKKO at cc.helsinki.fi.

Please credit this contribution to Professor Sture Forsén (Lund).

Sincerely yours,

Pekka Pyykkö
Professor of Chemistry

1992 Quadrupole Moments

Q/mb (= 10^{-31} m^2)

Nucleus	Q		Nucleus	Q		Nucleus	Q	
H-2	2.860(15)	m	Ga-69	170(30)	a	Gd-155	1270(30)	μ
Li-6	-0.82(4)	m	Ga-71	100(20)	a	Gd-157	1350(30)	μ
Li-7	-40.1	m	Ge-73	-173(26)	a	Tb-159	1432(8)	μ
Be-9	52.88(38)	a	As-75	314(6)	μ	Dy-161	2468(29)	μ
B-10	84.59(24)	a	Br-79	331(4)	a	Dy-163	2648(21)	μ
B-11	40.59(10)	a	Br-81	276(4)	a	Ho-165	3580(20)	π
C-11	33.27(24)	a	Kr-83	253(5)	a	Er-167	3565(29)	μ
N-14	20.2(3)	a	Rb-85	274(2)	a	Yb-173	2800(40)	μ
O-17	-25.58(22)	a	Rb-87	132(1)	a	Lu-175	3490(20)	μ
Ne-21	101.55(75)	a	Sr-87	335(20)	a	Lu-176	4970(30)	μa
Na-23	108.9(32)	a	Zr-91	-206(10)	a	Hf-177	3365(29)	μ
Mg-25	199.4(20)	a	Nb-93	-320(20)	μ	Hf-179	3793(33)	μ
Al-27	140.3(10)	a	Mo-95	-22(1)	a	Ta-181	3170(20)	π
S-33	-67.8(13)	a	Mo-97	255(13)	a	Re-185	2180(20)	π
S-35	47.1(9)	a	Tc-99	-129(6)	a	Re-187	2070(20)	π
Cl-35	-81.65(80)	a	Ru-99	79(4)	a	Os-189	856(28)	μ
Cl-37	-64.35(64)	a	Ru-101	457(23)	a	Ir-191	816(9)	μ
K-39	60.1(15)	a	Pd-105	660(11)	μ	Ir-193	751(9)	μ
K-40	-74.9(15)	as	In-113	799	a	Au-197	547(16)	μ
K-41	73.3(18)	am	In-115	810	a	Hg-201	386(49)	μ
Ca-41	-66.5(18)	a	Sb-121	-360(40)	a	Pb-209	-269(165)	a
Ca-43	-40.8(8)	a	Sb-123	-490(50)	a	Bi-209	-500(80)	π
Sc-45	-220(10)	a	I-127	-789	a	Rn-209	311(31)	a
Ti-47	290(10)	a	Xe-131	-120(12)	a	Fr-223	1170(10)	a
Ti-49	240(10)	a	Cs-133	-3.7(16)	a	Ac-227	1700(200)	a
V-50	210(40)	a	Ba-135	160(3)	a	Th-229	4300(900)	a
V-51	-52(10)	a	Ba-137	245(4)	a	Pa-231	-1720(50)	
Cr-53	-150(50)	a	La-138	450(20)	a	U-233	3663(8)	μ
Mn-55	330(10)	a	La-139	200(10)	a	U-235	4936(6)	μ
Co-59	420(30)	a	Pr-141	-58.9(42)	a	Np-237	3886(6)	μ
Ni-61	162(15)	a	Nd-143	-630(60)	a	Pu-241	5600(200)	a
Cu-63	-220(15)	μ	Nd-145	-330(30)	a	Am-243	4210	a
Cu-65	-204(14)	μs	Sm-147	-259(26)	μ	Es-253	6700(800)	a
Zn-67	150(15)	a	Sm-149	94(24)	μ			
			Eu-151	903(10)	μ			
			Eu-153	2412(21)	μ			

The values in this table are identical to those in ref. [1]. The original error limits are given and their meaning may vary. Methods: 'a' atomic, 'm' molecular, 's' solid-state, 'μ' muonic, 'π' pionic. 'XY': primary value from 'X', isotopic ratio from 'Y'.

References:

[1] P. Pyykkö and J. Li, Report HUKI 1-92, Helsinki (1992)
[2] P. Pyykkö, Z. Naturforsch. 47a (1992) 189.
[3] P. Raghavan, At. Data Nucl. Data Tables 42 (1989) 189.

varian associates / 3120 hansen way, box d-298 / palo alto, ca 94304-1030

NMR Applications Laboratory

January 12, 1993 (received 1/15/93)

Dr. Barry Shapiro
966 Elsinore Court
Palo Alto, CA 94303

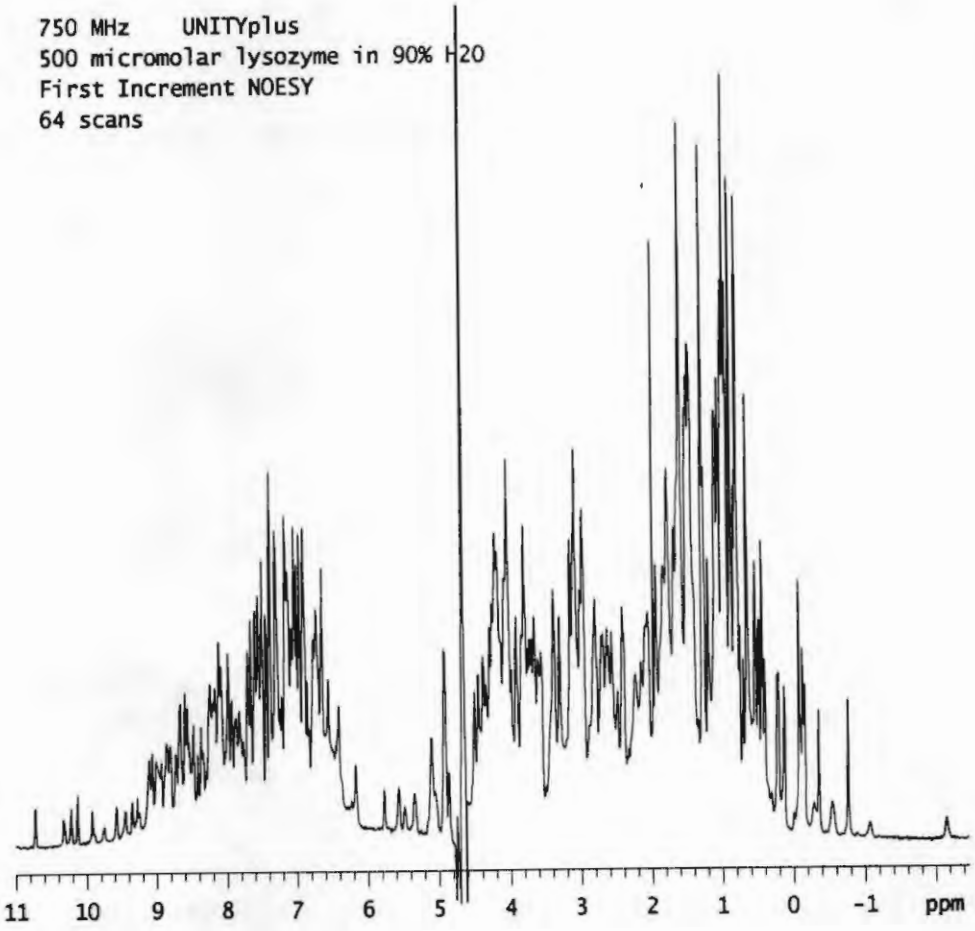
LongTerm Protein 2D in Water at 750 MHz

Dear Barry,

Now that 750 MHz is available it is important to assess its viability for the major application of very high-field NMR, that of biomolecular NMR. We tested this capability out last Fall using a new UNITY*plus* 750 on a dilute solution (500 micromolar lysozyme in 90% H2O) with the idea of checking the water suppression perfomance in the short-term, as well as the stability of water suppression over a longer run. To do this we set up a NOESY experiment to last 24 hours. The 750 MHz Oxford magnet shimmed with as much ease as our normal 500 or 600 MHz systems, resulting in a residual water lineshape shown in the first increment of the NOESY data set (Figure 1). Figure 2 shows the result of a 24 hour run having 32 transients per increment (400 complex t1 increments).

Figure 3 shows a comparison of a 4 hour run on 5mM lysozyme and the above data at 0.5 mM, for the fingerprint region. It is clear that even with a ten-fold dilution, the spectra contain essentially the same information. This demonstrated long-term stability is, of course, essential to be able to justify the significantly higher cost of the magnet.

Figure 1.



Sincerely Yours,

George Gray
Palo Alto Applications Lab

Peter Sandor
Darmstadt Applications Lab

varian associates / 3120 hansen way, box d-298 / palo alto, ca 94304-1030

Figure 2.

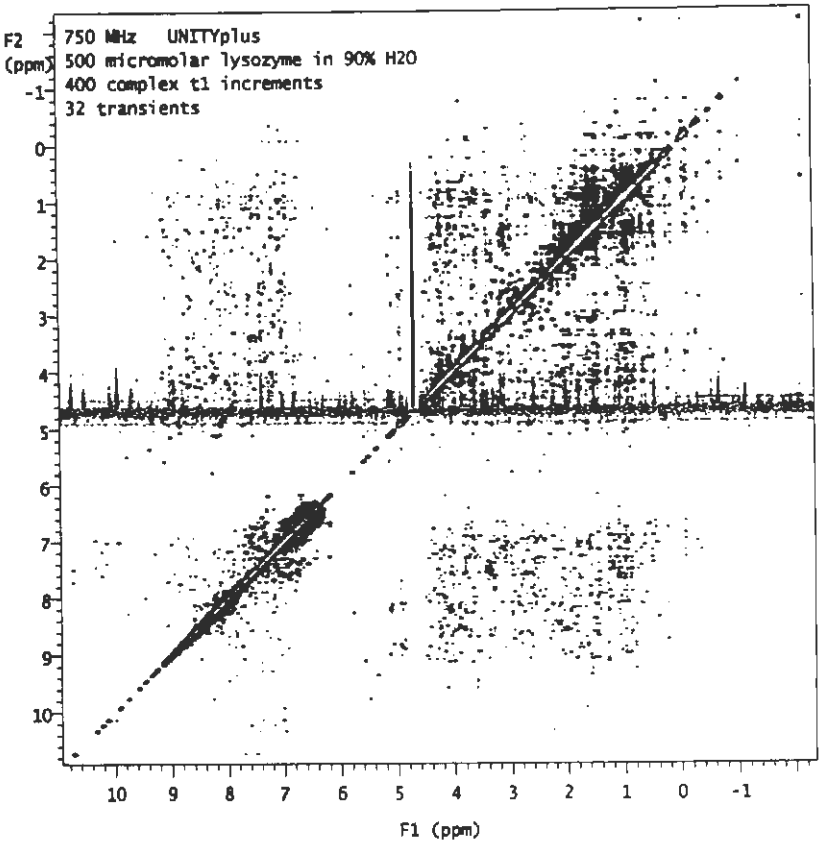
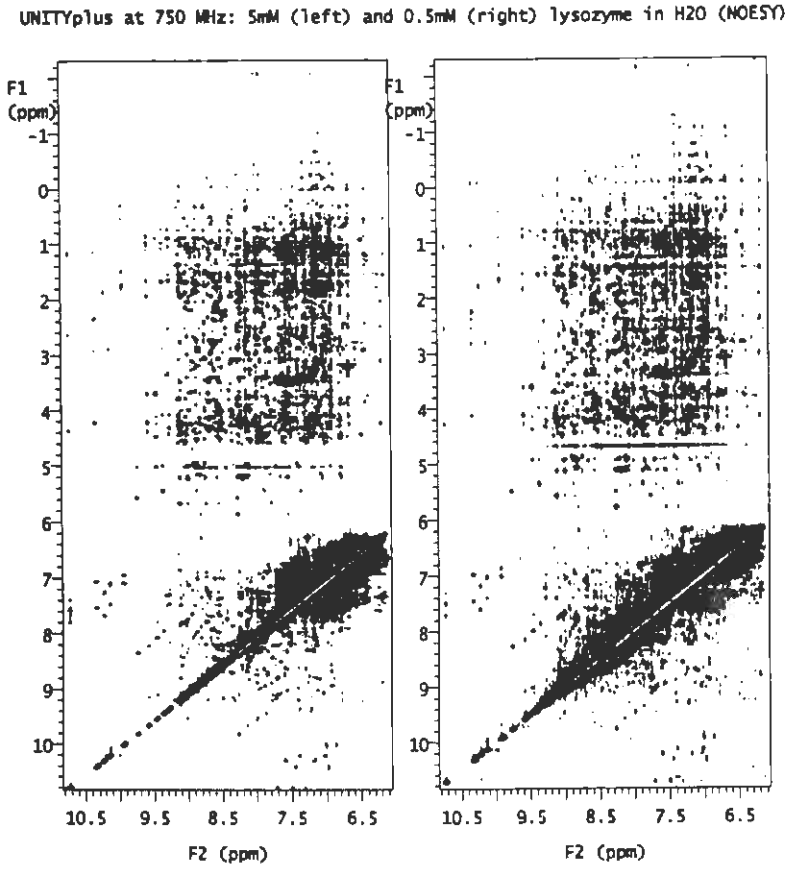


Figure 3.



New Z•SPEC®
Microsample Probes

Announcing a complete product line of high performance ^{1}H observe, broadband observe, indirect detection (ID), and triple resonance (IDT) microsample probes. Z•SPEC® Microsample probes feature extremely short PW90's and outstanding water suppression capability. The Microsample ID Probe and Broadband Observe Microsample Probe have full X channel tuning range (^{31}P-^{15}N).

APPLICATION

The Z•SPEC family of microsample probes allow you to complete the analysis of your quantity limited samples (140µl) in one-half the normal time compared to your standard 5mm probe. Shown on the next page are HMQC data from 12µg of cryptolepine (Figure 1), HMBC data from 35µg of cryptolepine (Figure 2), HMQC data from 140µg Digoxin (Figure 3), and TOCSY data from 140µg Digoxin (Figure 4).

These 500MHz spectra demonstrate the significant gain in absolute signal to noise performance and speed of analysis that can be achieved when using the Z•SPEC Microsample Inverse Detection Probe.

COMPATIBILITY

The top loading design of the Z•SPEC microsample probe assures convenient sample changing and compatibility with automatic sample changers. Z•SPEC probes interface directly to Bruker, General Electric, or Varian spectrometers operating at a ^{1}H frequency of 200, 250, 270, 300, 360, 400, 500, or 600 MHz.

CUSTOMER SUPPORT

The staff of the Z•SPEC probe group include applications specialists who are available to install and support our products in your laboratory. For more information about Z•SPEC NMR probes, contact our marketing department.

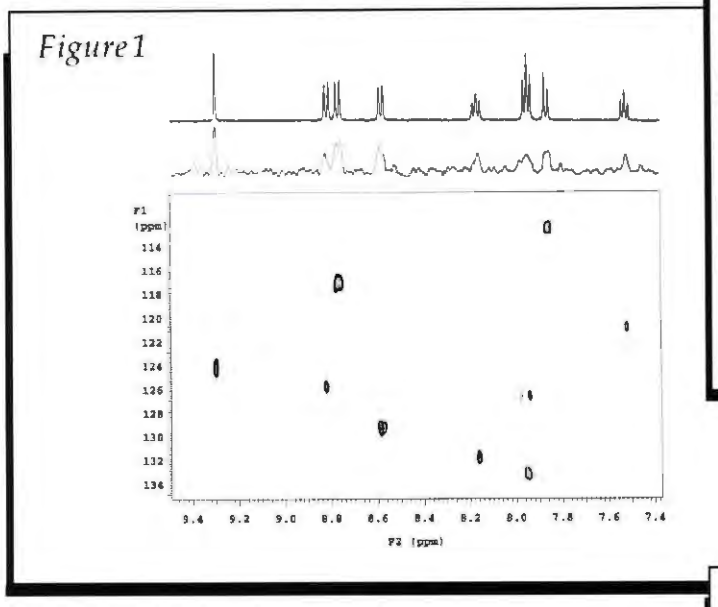
NALORAC

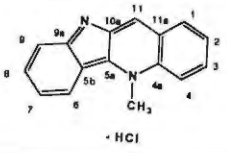
837 Arnold Drive, Suite 600, Martinez, CA 94553
Tel: (510) 229-3501 • FAX 510.229.1651

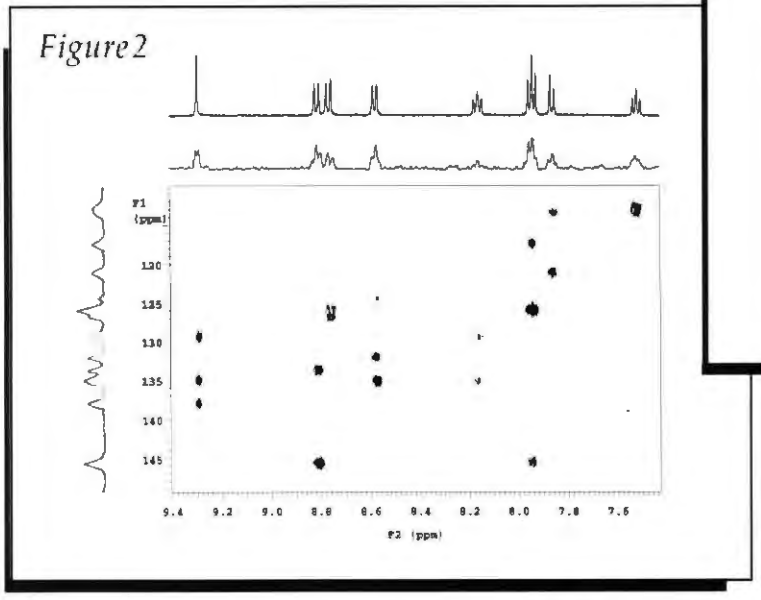
Z·SPEC® Microsample Spectra

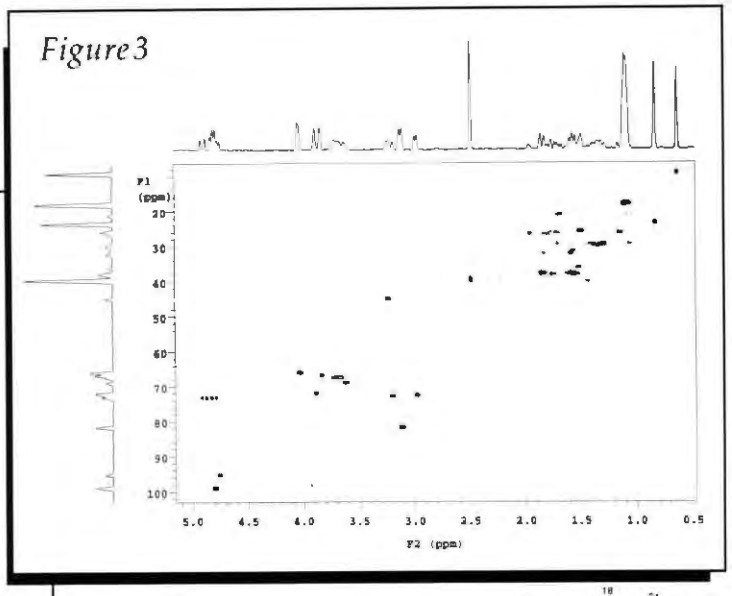
Figure 1: HMQC Spectra of 12µg of cryptolepine obtained in 16 hours with Z•SPEC MID500 probe. Normal ^1H spectrum (256 transients) for the 12µg sample plotted on top.

Figure 2: HMBC Spectra of 35µg cryptolepine obtained in 22 hours with Z•SPEC MID500 probe. Aromatic F_2 window. Normal ^1H spectrum (64 transients) for 35µg sample plotted on top.









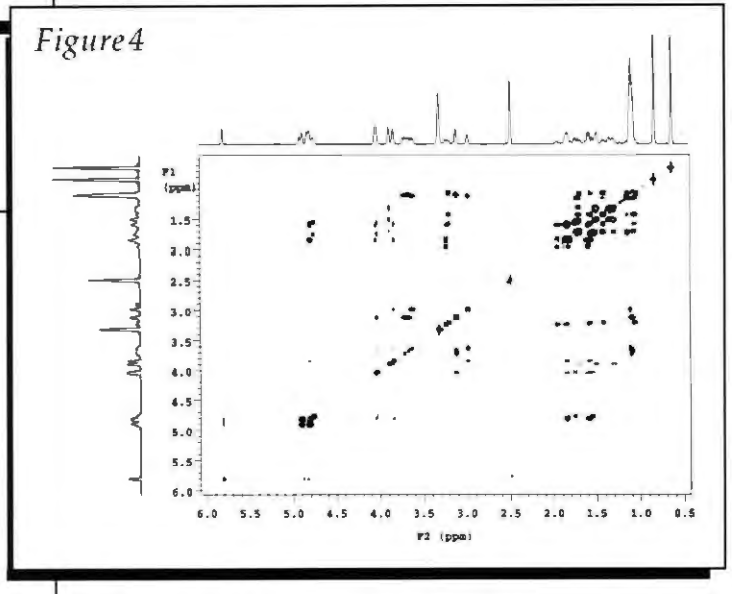


Figure 3: HMQC Spectra of 140µg Digoxin obtained in 14.5 hours with Z•SPEC MID500 probe.

Figure 4: TOCSY Spectra of 140 µg Digoxin obtained in 58 minutes with Z•SPEC MID500 probe.

Please review the following publications for additional examples of results obtained with Z•SPEC Microsample Probes: Micro Inverse-Detection: A Powerful Technique for Natural Product Structure Elucidation, Ronald C. Crouch and Gary E. Martin, *Journal of Natural Products*, **55 (9)**, pg 1343-1347 (1992); Comparative Evaluation of Conventional 5mm Inverse and Micro-Inverse Detection Probes at 500MHz, Ronald C. Crouch and Gary E. Martin. *Magnetic Resonance in Chemistry*. In press.

NALORAC

837 Arnold Drive, Suite 600, Martinez, CA 94553
Tel: (510) 229-3501 • FAX 510.229.1651

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service

National Institutes of Health
National Institute on Aging
Gerontology Research Center
4940 Eastern Avenue
Baltimore, Maryland 21224

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

January 7, 1993
(received 1/14/93)

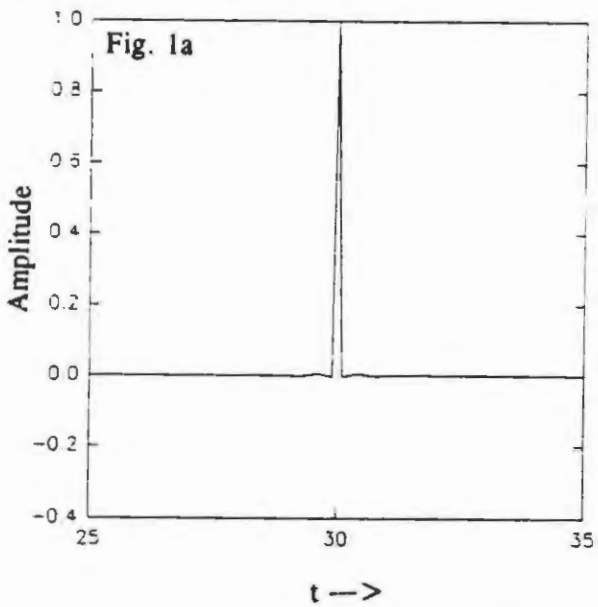
Simulated Echoes

Dear Dr. Shapiro:

While a vector picture of the 90-τ-180 echo (sequence 1) conveys very nicely how that echo comes about, the same cannot be said for the 90-τ-90 (sequence 2) or 90-τ_1-90-τ_2-90 (stimulated echo, sequence 3) sequences. As a pedagogic device to aid in discussions of these sequences, therefore, I calculated the time-domain signal resulting from them, thereby directly simulating the echoes.

Starting from an initial density matrix I_x, the density matrix at a time t after the second pulse in sequence 1 is $\rho(t)=I_x\sin\{\Omega(\tau-t)\} + I_y\cos\{\Omega(\tau+t)\}$ for an isochromat at offset Ω, and with both pulses x-phase. So, $FID(\Omega,t)=\sin\{\Omega(\tau-t)\} + i*\cos\{\Omega(\tau+t)\}$, and, as all textbooks state, the fact that this expression is independent of Ω at $t=\tau$ leads to echo formation. To see the echo numerically, all that is required is to sum the FID's for a range of Ω's: $FID(t)=\Sigma\, p_i FID(\Omega_i,t)$, where p_i is a probability distribution describing the number of isochromats of frequency Ω_i. Similarly, for sequence 2, and again with x-phase pulses, one finds $FID(\Omega,t)=\cos(\Omega t)\sin(\Omega\tau) + i*\sin(\Omega t)\sin(\Omega\tau)$, while for sequence 3, $FID(\Omega,t)=\cos(\Omega t)\cos(\Omega\tau_2)\sin(\Omega\tau_1)-\sin(\Omega t)\cos(\Omega t_1) + i*\sin(\Omega t)\cos(\Omega\tau_2)\sin(\Omega\tau_1)+\cos(\Omega t)\cos(\Omega t_1)$. All of these FID's are simple to compute since the pulses involved are 90's or 180's.

In the following, we will assume that there are a total of N_0 isochromats, ranging from Ω_L to Ω_U, and spaced in frequency by $\Omega_{INT}=(\Omega_U - \Omega_L)/N_0$. For simplicity, p_i will be taken as unity, and T_2 relaxation will be neglected. As all of the pulses are considered to be x-phase, only the y-component (that is, the refocussing component) of the FID's are displayed.



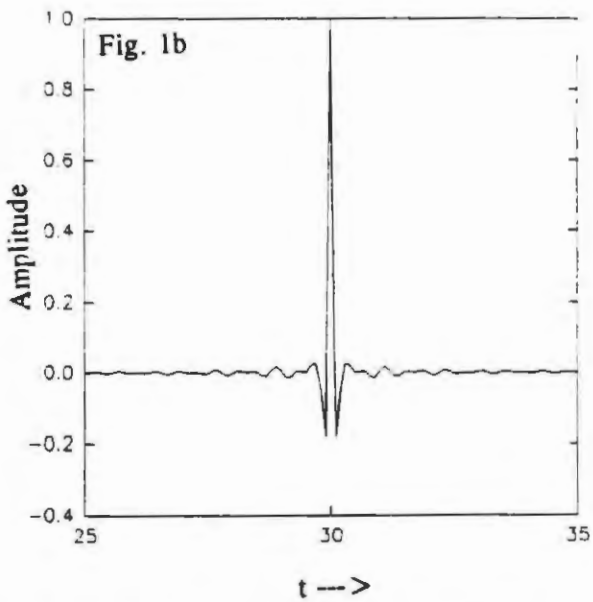


Figure 1a (left). Sequence 1, with $\tau=30$, $\Omega_L=10$, $\Omega_U=1010$, $\Omega_{INT}=0.0625$, and $N_0=16{,}000$. A clean echo of amplitude 1 (recovery of full intensity) occurs at $t=\tau$. Figure 1b (right). Same as Fig. 1a, except that $\Omega_U=110$ and $N_0=1600$. Note that with a smaller range of isochromat frequencies, the breadth of the echo is increased. The distortions seen at what should be the sharp edges of the echo signal (c.f. Fig. 1a) correspond to Gibbs phenomenon. That is, they arise from the approximation of a sharp feature (the echo) with a Fourier series comprised of terms of limited frequency range. Decreasing Ω_{INT}, but leaving Ω_U unchanged by increasing N_0, does not diminish these oscillations. Analogous behavior as a function of Ω_U is seen with all three sequences.

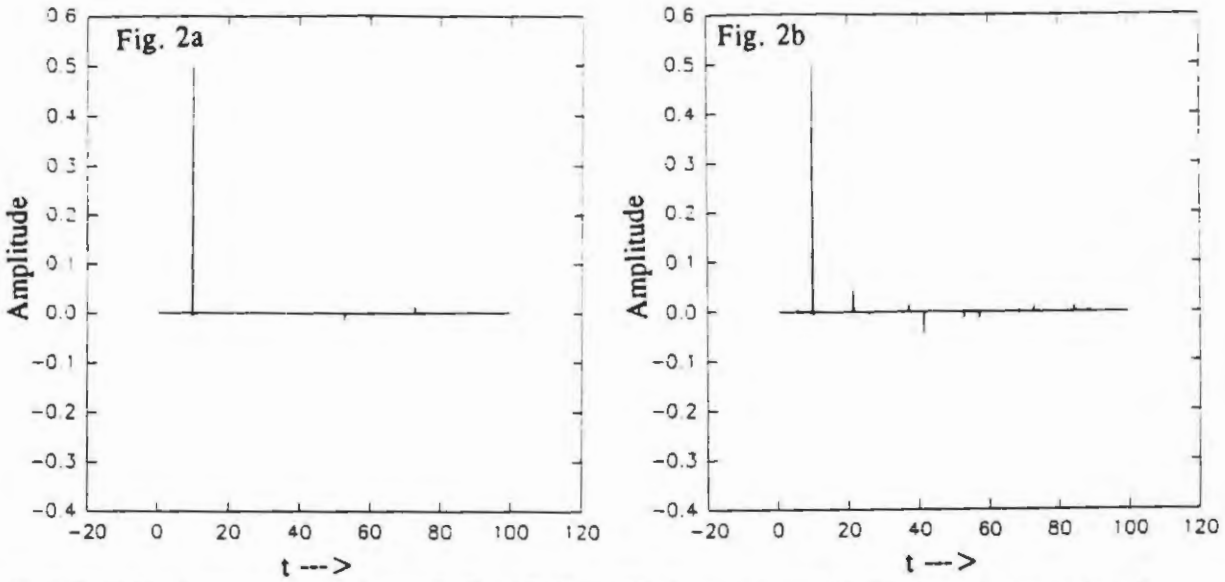


Figure 2a (left). Sequence 2, with $\tau=10$, $\Omega_L=10$, $\Omega_U=650$, $\Omega_{INT}=0.1$, and $N_0=6400$. A clean echo of amplitude 0.5 (recovery of only half of the full intensity, as expected for this sequence) occurs at $t=\tau$. Figure 2b (right). Same as Fig. 2a, except that $\Omega_{INT}=0.4$, and $N_0=1600$. With the same range of Fourier components, the echo is still sharp. However, with a limited number of isochromats within that range, spurious echoes (accidental refocussing) occurs. Analogous behavior as a function of Ω_{INT} is seen with all three sequences.

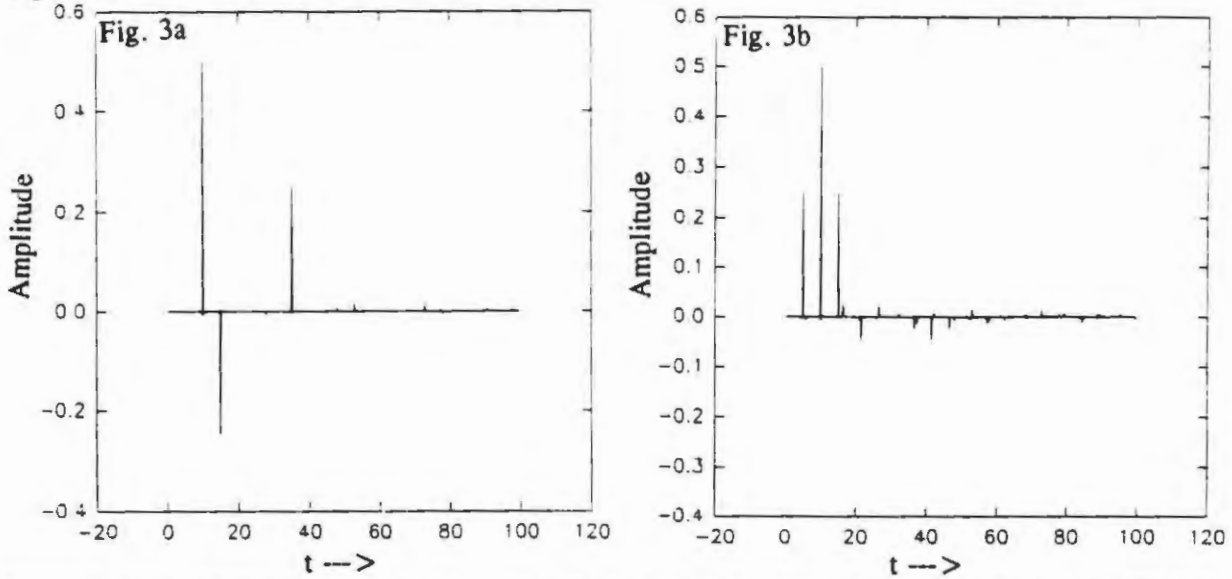


Figure 3a (left). Sequence 3, with $\tau_1=10$, $\tau_2=25$, $\Omega_L=10$, $\Omega_U=650$, $\Omega_{INT}=0.1$, and $N_0=6400$. A stimulated echo of amplitude 0.5 (recovery of only half of the full intensity, as expected for this sequence) occurs at $t=\tau_1$. The secondary echoes predicted in Hahn's 1950 paper[1] also appear. Fig. 3b (right). Sequence 3, with $\tau_1=10$, $\tau_2=5$, $\Omega_L=10$, $\Omega_U=650$, $\Omega_{INT}=0.4$, and $N_0=1600$. The stimulated and secondary echoes are seen as expected, as are the spurious echoes resulting from the small number of isochromats.

Reference: 1. E. L. Hahn. Spin Echoes. Physical Review 80, 580-594 (1950).

Yours sincerely,

Richard G. S. Spencer (NIH/NIA; GRC 4D-13)

Please credit this contribution to Gunther L. Eichhorn's subscription.

Varian NMR Users

RELIABILITY AND MAINTENANCE A CONCERN?

PseudoCorp provides

Repair Services and Parts for :

CFT-20

FT-80

FT-80A

XL-100

XL-200

PseudoCorp specializes in providing quality maintenance services for Varian processors and associated peripherals. PseudoCorp also offers LOW COST, HIGHLY RELIABLE, NEW TECHNOLOGY replacement elements for the Varian 620 and V77-200 systems in your NMR's console. A partial list of the new devices available include:

- **PseudoCorp 2100x processor and memory - a single board replacement for the V77-200 or 620 series processor including 1 megabyte of memory.**
- **PseudoMem 100 - a single board CMOS battery backed replacement for 32k 620 series memory (priced lower than the repair cost of a 4k memory stack).**
- **PseudoFloppy - a replacement for the Varian 8" floppies which creates MS-DOS compatible files. The PseudoFloppy includes an operator's console and pre-stored bootstrap capability. Processor diagnostics are also optionally available.**

We want to restore your system to like-new reliability. Call us now.

(See reverse for details)

Products and Services

- **PDM2100x [tm] Series Processor**
  - Direct single board replacement processor for Varian 620i, l , f, V72, V73, V74, V75, V76, V77-200, 400, and 600 series processors.
- **PseudoStore 7000 [tm]**
  - 100% Software and hardware compatible floppy disk replacement. IBM PC compatible based system emulates the original equipment floppy system while providing the following enhanced features:
  - All data is available in PC readable form. Each floppy is just a file under MS-DOS.
  - Computer Operator's console with complete processor diagnostics option.
  - No floppy disks are involved, except as data backup - PseudoFloppies (Files on the PC hard disk) are used to store all information.
  - Complete floppy system uses standard, easy to find parts.
- **PseudoMem 100 [tm]**
  - Solid state replacement for the core memory used in the older console processors. Battery backup assures complete compatibility with existing memory. Very low power, high reliability CMOS static rams provide years of trouble-free service.
- **8" to PC compatible floppy transcription service**
  - For as low as $2.00 per 8" floppy, PseudoCorp will copy your Varian disks to 5 1/4" or 3 1/2" PC compatible floppies. ($50.00 minimum order)
- **Computer Service**
  - Skilled field service engineers.
- **Special -- First Quarter 1993**
  - 10% Discount on PseudoStore 7000 [tm] (Must take delivery by 3/31/93)

For More Information, Or To Order Call

PseudoCorp
Data Machines Group
716 Thimble Shoals Blvd.
Newport News, VA 23606
(804) 873-4977 FAX: (804) 873-2154

Bruker Instruments, Inc.

Fortune Drive
Manning Park
Billerica, MA 01821
(508) 667-9580
Fax: (508) 667-3954

BRUKER

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

February 5, 1993
(received 2/6/93)

"ROUTINE" 750 MHz NMR SPECTROSCOPY

Dear Barry:

In October 1991, Bruker reported in TAMU on the first prototype 750 MHz magnet, and in December 1992, we reported the first high-resolution high-dispersion spectra from our AMX 750 production spectrometer. Since then our engineers and application scientists in the AMX 750 demo lab have been running spectra around the clock to explore the capabilities of this next magnet and spectrometer generation.

It appears that the magnet drift rate has settled well below 10 Hz per hour. Due to the magnet design objective of a very large homogeneous volume, the 1 % $CHCl_3$ non-spinning lineshape was better than 5/8 Hz using the latest BOSS™ 2 shim system. Our 750 MHz magnet is the first high-resolution magnet which uses Bruker's revolutionary magnet pressure and temperature stabilization technology, and indeed the overall stability of the 750 magnet far surpasses any previous high-field NMR magnet.

Water suppression is demonstrated on 5 mM lysozyme in 90% H_2O/10% D_2O with a) simple presat, b) as a first increment of a 2D-NOESY-presat, and finally c) the 2D NOESY with presat. Figures 1 a, b, and c show the excellent water suppression, absence of artifacts and excellent S/N and resolution of the AMX 750.

A practical demonstration of the increased sensitivity and dispersion at 750 MHz is given by some impressive results in body fluids analysis. Figure 2 shows 750 MHz spectra of human urine after dosage of 200 mg of flurbiprofen (sample courtesy of Jeremy Nicholson, Birkbeck College, U. of London, UK). Figure 2a is the first scan of a NOESY with presat, and Fig. 2b is the DQF-COSY of this sample. The increased dispersion compared to 600 MHz spectra clearly helps in resolving spectral overlap and ambiguities.

We are looking forward to showing more 750 MHz results to the NMR community at ENC. See you in St. Louis !

With best regards,

Frank H. Laukien

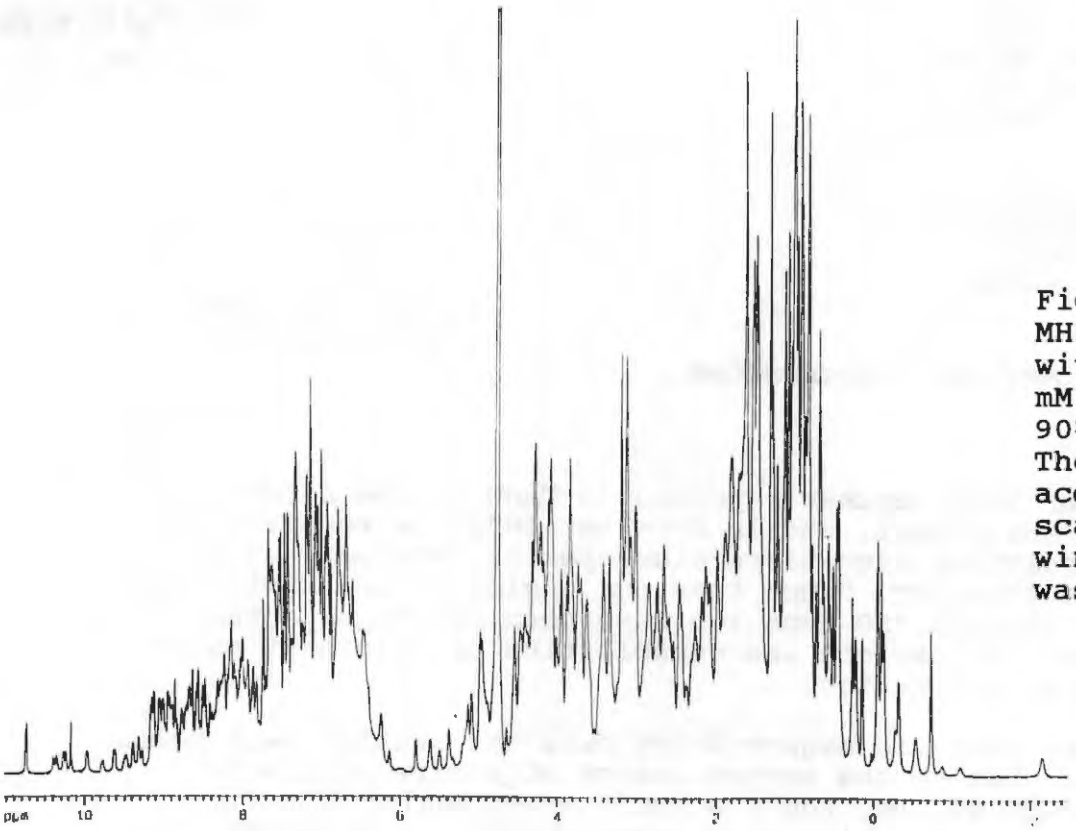


Figure 1a: 750 MHz ^1H spectrum with presat of 5 mM lysozyme in 90% H_2O/10% D_2O. The spectrum was acquired with 16 scans, and no window function was applied.

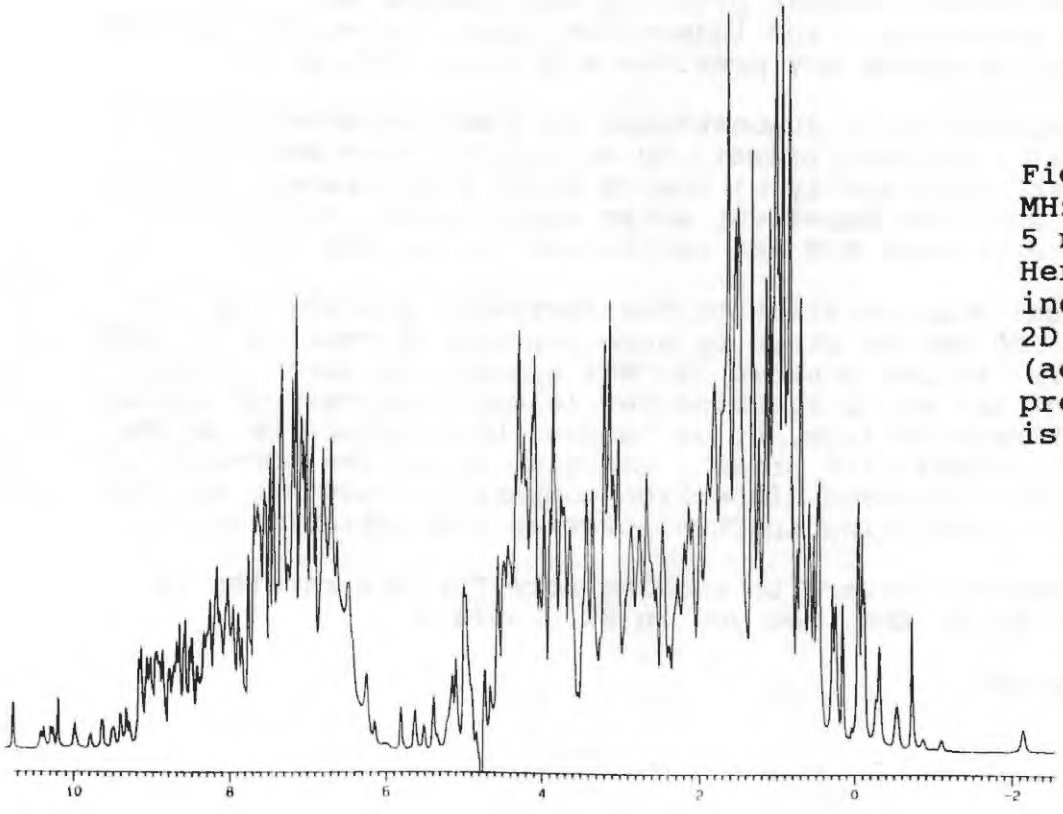


Figure 2b: 750 MHz spectrum of 5 mM lysozyme. Here the first increment of the 2D NOESY (acquired with presaturation) is shown.

BRUKER

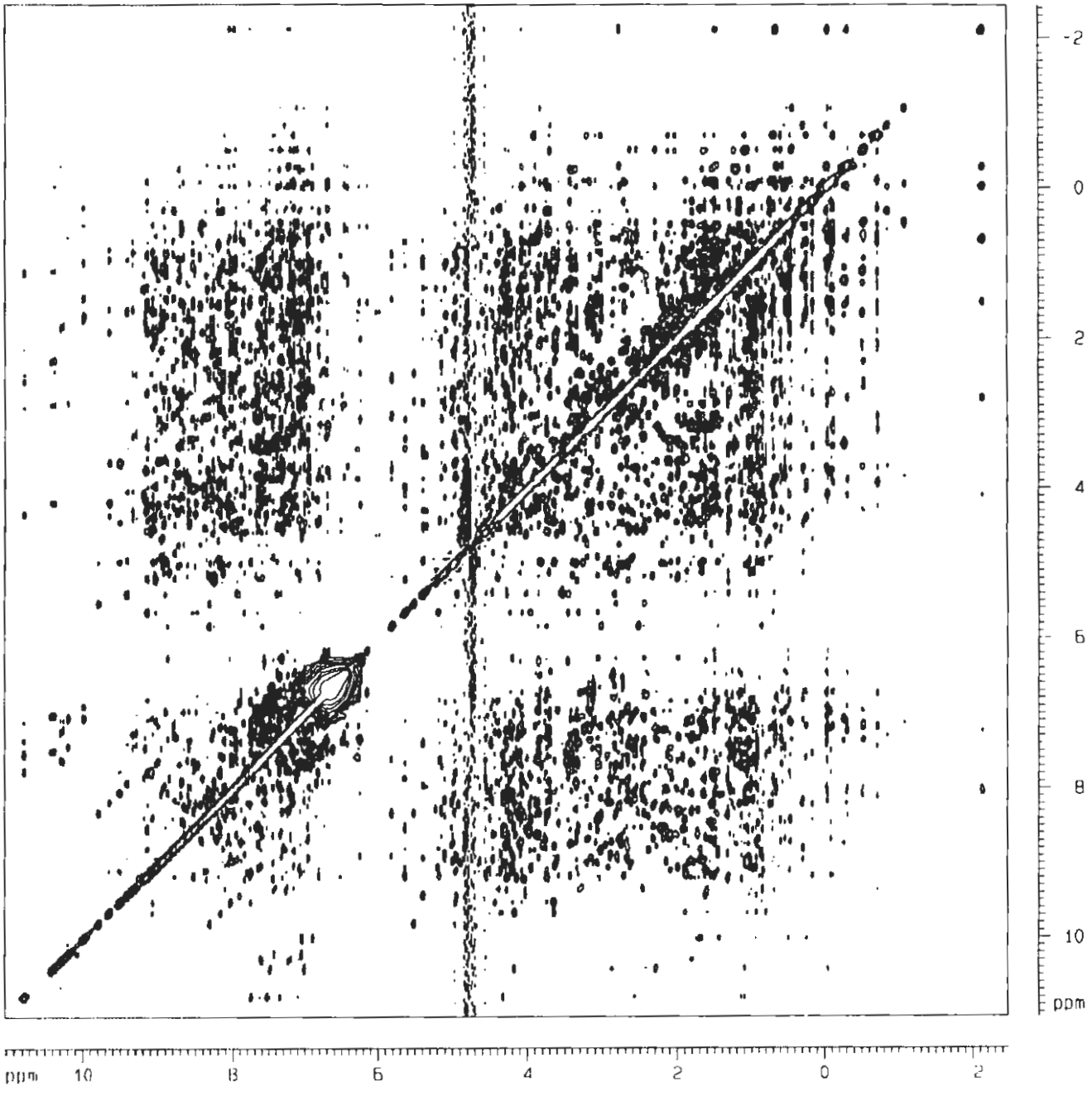


Figure 1c: 750 MHz NOESY spectrum with presaturation. The sample is 5 mM Lysozyme in 90% H_2O/10% D_2O. The spectrum was acquired with 16 scans and 512 increments.

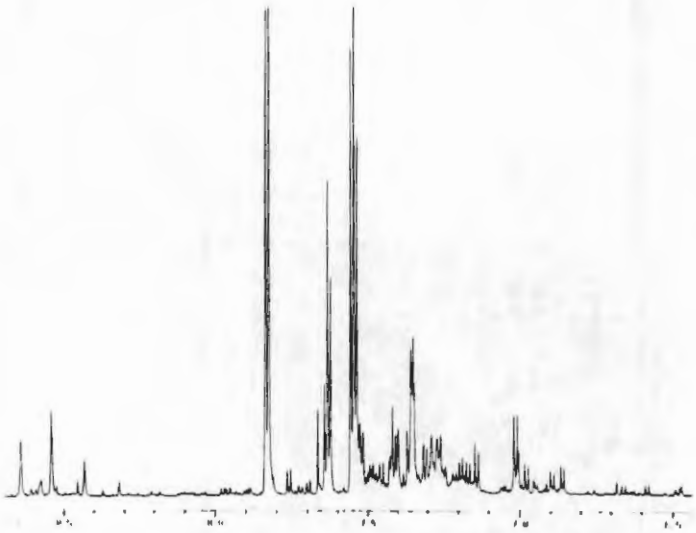


Figure 2a:
750 MHz ^{1}H NOESY spectrum with presat. The sample is human urine after a 200 mg dose of flurbiprofen.

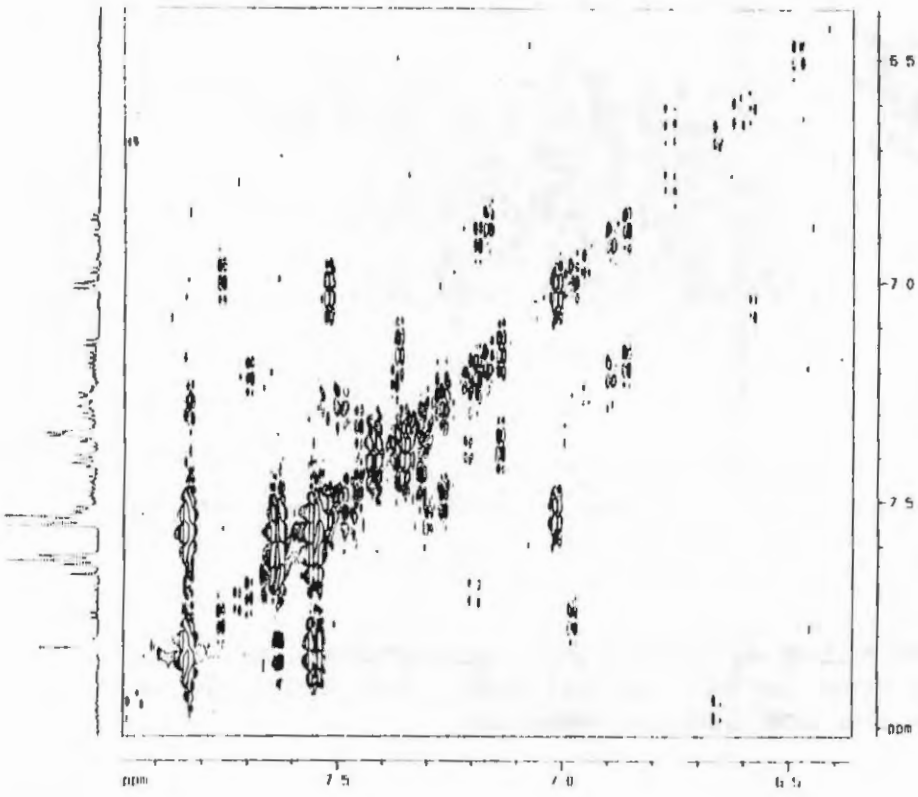


Figure 2b:
750 MHz DQF COSY spectrum. The sample is as above.

Table of Contents, cont'd.

* * * * *

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. 415 (April) ---------- 19 March 1993
No. 416 (May) ---------- 23 April 1993
No. 417 (June) ---------- 21 May 1993
No. 418 (July) ---------- 25 June 1993

The Newsletter's fiscal viability depends very heavily on the funds provided by our Advertisers and Sponsors. Please do whatever you can to let them know that their support is noted and appreciated.

Mailing Label Adornment: Is Your Dot Red?

If the mailing label on your envelope of this issue is adorned with a large red dot or circle: this decoration means that you will not be mailed any more issues until a technical contribution has been received by me.

PLEASE **Page Length Instruction**

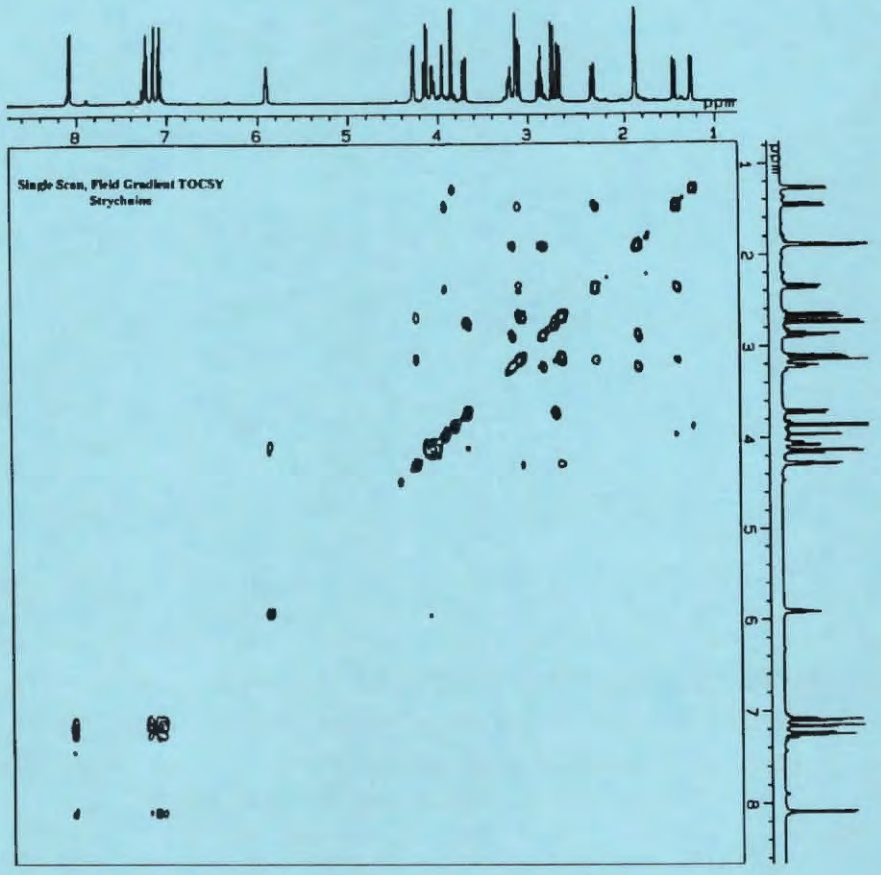
Attention overseas subscribers: If you must use paper which is longer that 11", *please* take care that all material (including signatures, addresses - everything!) ends no more than 10" from the top of each of your pages. It is costly to make reductions, and henceforth I reserve the right to chop the excess length off any page, no matter what the result. Beware of the dreaded guillotine! Your cooperation in this matter will be greatly appreciated.

WANTED: *An Advertiser for this inside back cover page!*

NMR

FROM JEOL USA

Gradient Probes



The above data is a 512 by 512 *TOCSY* spectrum and was obtained on an **Alpha**- 500 in less than 5 minutes with **JEOL**'s gradient probe. This same probe is also designed to do reverse and water suppression experiments. Pulse shaping, three channel operation, dynamic Rf control, matrix shims, as well as unsurpassed field reliability are all standard with the **Alpha**.

ALPHA FIRST IN PERFORMANCE, FIRST IN TECHNOLOGY

JEOL, USA
11 Dearborn Rd.
Peabody, MA 01960
508/535-5900
FAX 508/535-7741

JEOL, NJ
23 E. Brunswick Dr
East Brunswick, NJ
908/254-7026
FAX 908/254-8850

JEOL, CA
3500 West Bayshore Rd
Palo Alto, CA 94303
415/493-2600
FAX 415/493-0581

JEOL, IL
9801W. Higgins Rd Suite 220
Rosemont, IL 60018
708/825-7164
FAX 708/696-2559

JEOL NMR

Soquelec, Ltd.
5757 Cavendish Blvd
Suite 101
Montreal, Quebec
Canada H4W2W8
514/482-6427
FAX 514/482-1929

JEOL, DE MEXICO
Insurgents Sur #953
Col. Napoles
03810 Mexico D.
525/515-2616
FAX 525/515-3261