

# NMR

## NEWSLETTER

No. 347

August 1987

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# TAMU NMR Newsletter

Editor/Publisher: Bernard L. Shapiro

Mailing address for all correspondence: 966 Elsinore Court, Palo Alto, California 94303, U.S.A. (415) 493-5971

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Updated 31 July 1987  
~~26-June-1987~~

## Implications of the Above Letterhead and Address

1. The NMR Newsletter will continue, into the long-term, indefinite future, without significant interruption. It will in fact continue as the TAMU NMR Newsletter, and with the undersigned continuing as Editor/Publisher.

2. New mailing address: effective 1 September 1987, the new address given above should be used for all correspondence, enquiries, etc., including the transmittal of technical contributions, enquiries, and checks. Please do not send any mail to the Texas A&M University address after 1 September 1987.

3. Newsletter Policies. The operating policies and procedures for the TAMU NMR Newsletter will not change. After what will, I hope, be a brief period of ironing out logistic problems, the Newsletter will remain in its present form in virtually all respects. As time goes along and we are able to do so, there will be certain cosmetic changes in the appearance of the Newsletter, but these would probably be instituted were I not moving. To reiterate, our Newsletter participants/subscribers/sponsors/advertisers will enjoy the same product, service, opportunities/problems, etc., as at present.

No immediate change of subscription rates is being made, and the invoices for the October 1987 - September 1988 year which were mailed out early in August are at the same rates as we have been able to maintain for the past three years. The Newsletter will continue to be wholly self-supporting, so we will continue to depend - even more heavily - on the generosity and participation of our loyal Sponsors and Advertisers. Please let me know promptly if you have not received your 1987-88 invoice by the time you read this notice.

- continued. . .



4. For those who have an active curiosity about such non-cosmic matters, the above changes of geography reflect the fact that as of September 1, 1987, I will be participating in Texas A&M University's "Early Retirement Program With Modified Service". The "Modified Service" part consists, inter alia, of continuing to serve as Editor/Publisher of the NMR Newsletter as the TAMU NMR Newsletter. (I will also be continuing to serve as a North American Editor of Magnetic Resonance in Chemistry.).

Texas A&M University will be providing the organizational matrix through which the Newsletter will operate, and while funds will need to be mailed to me so that I can keep the appropriate records, etc., the checks will still need to be made out to Texas A&M University, and all funds will be transmitted by me to the University for deposit; check your 1987-88 invoices for details.

5. The Future of the TAMU NMR Newsletter: I hope and expect to operate this Newsletter for many years, with the gradual, incremental type of development which has characterized it for the last twenty-nine years. I do not contemplate any major changes, although suggestions for the continued development and improvement of the Newsletter are, as always, most welcome.

*BL Shapiro*

# TEXAS A&M UNIVERSITY

# NMR

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**FORTHCOMING NMR MEETINGS**

**FACSS XIV** - October 4-9, 1987; Detroit, Michigan; For information, contact Dr. Stephen J. Swarin, Publicity Chairman, Analytical Chemistry Department, General Motors Research Labs, Warren, Michigan 48090-9055, 313-986-0806.

**Symposium on the High Resolution NMR of Solids** - October 15, 1987; Washington University, St. Louis, Missouri. See page 42 of Newsletter #346, July 1987 for additional information.

**Symposium on Resonance in Perspective - A Tribute to Professor Richard E. Norberg** - October 16-17, 1987; Washington University, St. Louis, Missouri. See page 43 of Newsletter #346, July 1987 for additional information.

**Magnetic Resonance Spectroscopy for Clinicians** - October 18, 1987; San Francisco, California; University of California Medical Center, San Francisco, California; For registration information, call (415) 476-5808.

**1987 Materials Research Society, Fall Meeting** - Nov. 29-Dec. 5, 1987; Boston Marriott Hotel, Boston, Massachusetts. Short course on NMR Spectroscopy - Wednesday, December 2. Course Instructor: James P. Yesinowski (Cal Tech). For further details, contact: Materials Research Society, 9800 McKnight Road, Suite 327, Pittsburgh, Pennsylvania 15237.

**Fritz Haber International Workshop on Modern Techniques in Magnetic Resonance** - December 13-17, 1987; Weizman Institute of Science, Rehovot, Israel; See page 7 of Newsletter #341, February 1987, for additional information.

**NMR-88** - February 14-18, 1988; Thredbo Alpine Hotel, Thredbo, N.S.W. Australia. Chairman: Dr. L.R. Brown, The Australian National University. For further information, contact: Leslie Harland, Research School of Chemistry, The Australian National University, Canberra, A.C.T. 2601, Australia. Telex: AA62172. Facsimile: (61-62)-49-7817. Telephone: (61-62)-49-2863.

**29th ENC (Experimental NMR Conference)** - April 17-21, 1988; Rochester, New York; Chairman: Professor Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, (215) 898-6459. For information, contact Professor Edward O. Stejskal, ENC Secretary, Department of Chemistry - Box 8204, North Carolina State University, Raleigh, North Carolina 27695-8204; telephone (919) 737-2998.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence  
 Should be Addressed to:

Dr. Bernard L. Shapiro  
 TAMU NMR Newsletter  
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**DEADLINE DATES**

No. 349 (October) --- 25 September 1987  
 No. 350 (November) ---- 23 October 1987

## THE UPJOHN COMPANY

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July 7, 1987

(Received 21 July 1987)

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

INDIRECT DETECTION ON BRUKER AM SPECTROMETERS

Dear Professor Shapiro:

This letter describes a microprogram modification necessary to do the indirect detection experiment on a Bruker AM Spectrometer. The indirect detection mode can be used for HOHAHA, HMQC, or HMBC. Our spectrometer is a four-year-old AM300 which has been upgraded with the process controller. The upgrade includes an additional +5 volt power supply in the Aspect 3000 and new Transmitter F1, Transmitter F2, and PTS interface boards. The new version of the Transmitter F2 board has additional circuitry installed to allow the generation of the 6.15 MHz IF reference for the Receiver. In normal mode, the IF reference is generated on the F1 board, and for proton detection the receiver is kept phase coherent with the BSV transmitter and O1 offset frequency by this pathway. For indirect detection, the decoupler is used as a variable power transmitter. In order to make the receiver coherent with the decoupler and O2 offset frequency, the IF generation circuitry on the F2 board is used. On new Bruker AM consoles, the IF generation is routed to the F2 board by reversing a plug on the right side of the spectrometer. In addition, this plug switches a relay to bypass frequency mixing in the B-SV7 LO-Signal, thus using the proton frequency for detection in the receiver. Our method of doing this is to remove the cables from the R and V openings of the F1 Burndy connector and place two coaxial jumpers from these cables to the R and V openings of the F2 Burndy connector. We have a B-SV6 and can bypass frequency mixing by switching the relays involved in the LO-Signal pathway [<sup>1</sup>], or by using Bruker's method and taking the Mixing Unit 2 out of slot number three and replacing it with the LO X 3 unit from slot number four. With the LO X 3 unit residing in slot three and PR set for an X nucleus amplifier (PR=L1 or H1), the receiver will detect the proton frequency. Our setup at the preamplifier housing involves removing the F1 BNC cable and connecting it

---

<sup>1</sup> L.D. Field and A.K. McPhail, J. Magn. Reson. 67, 364-366 (1986).

directly to the cable from the X-nucleus fitting on the probe, thus bypassing the X-nucleus preamplifier. The F2 BNC cable is disconnected from Decoupler In and reconnected at F1 In on the side of the housing. This arrangement eliminates the need for a directional coupler.

After getting the hardware configured correctly, there remains a software problem (at least with versions DISR861 and DISRVK41 - we don't know whether the 1987 version will correct it). The problem manifests itself by phase distortion in the spectrum if more than one transient is taken. With a one-pulse experiment, it is obvious that the FIDs don't add equally during phase cycling.

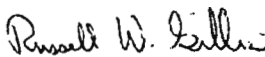
The software assumes that the spectrometer is always in normal mode. When using 'GO=n' with no associated phase program, the Detection Reference Phase is set to 0 during the second half of DE. When using discrete commands ('ADC' and 'RCYC' instead of the macro 'GO=n'), a delay, e.g. D5, must be substituted for DE/2. A phase program must be specified with the second DE/2 period to set the Detection Reference Phase for the receiver. These standard program methods work as long as the receiver reference phase comes from the 01 offset frequency (normal mode), because the software resets 01.

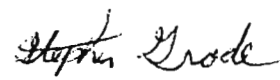
For indirect detection, the receiver gets its reference phase from the 02 offset frequency. As 02 and the decoupler go through phase cycling, the program resets 01 for detection each time. However, the receiver, being tied to 02, continues to use the decoupler phase cycling for its detection. The solution to this problem is to insert a dummy decoupler pulse prior to ADC or GO to reset the 02 phase for detection. We use P8:D PH8 to set the receiver phase and specify a time of P8=0 and a phase program of PH8=0. While it is not possible to reset the phase in 0 seconds, we find that this parameter works well. The phase change probably takes on the order of tens of nanoseconds to propagate.

Testing for proper behavior of the Detection Reference Phase is accomplished by using a single-shot, single-scan experiment. Take one scan and phase the reference spectrum. Change the phase program for either the decoupler or the receiver by 90 degrees and take another single scan. After phase correcting the spectrum with the same constants as the reference spectrum (PK command), this test spectrum should differ from the reference spectrum by 90 degrees. Without the dummy pulse to reset the phase to a fixed value in indirect detection, the test spectrum is always the same phase as the reference spectrum.

Please credit this contribution to Neil MacKenzie's account.

Sincerely,

  
Russell W. Gillis

  
Stephen H. Grode

;H90REV. AUR

; CALIBRATION OF 1H-90-DEGREE PULSE IN REVERSE MODE

```

1 ZE
2 D1 S1 CW DD ; SET DECOUPLER FOR PULSING WITH POWER S1
3 P1:D PH1 ; 1H PULSE FROM THE DECOUPLER
4 D5 ; DE/2
5 D5 ; DE/2, OPEN DIGITIZER
   P8:D PH8 ; SET DETECTION REFERENCE PHASE
6 D6 ADC ; DIGITIZE FOR TD+DW TIME = AQ
7 RCYC 2 PH2 ; RECYCLE, DIGITIZER PHASE SET
8 EXIT

PH1=0 ; DECOUPLER PULSE PHASE
PH2=0 ; DIGITIZER PHASE
PH8=0 ; RECEIVER DETECTION PHASE

```

```

; NS=1
; PW=RD=0
; D1 = RELAXATION DELAY
; P1 = 90 DEG DEC PULSE AT S1
; D5 = DE/2
; D6 = AQ
; P8 = 0
; *****
; SET DETECTION SWITCH TO REVERSE
; *****

```

---

Biological NMR Post-Doctoral Position, available immediately. Applications will be considered from candidates who have demonstrated experience in at least three of the five techniques listed here: 1) 2D NMR of peptides or oligonucleotides, 2) NMR pulse program development, 3) computer programming in C and FORTRAN, 4) protein or receptor isolation and purification, and 5) conformational modeling using computer graphics or molecular dynamics. The research area will be the development and application of novel 2D NMR methods for studying biorecognition phenomena. A C.V., letter of intent, and three letters of reference should be directed to Niels H. Andersen, Department of Chemistry, University of Washington, Seattle, WA 98195. The University of Washington is an equal opportunity employer. The closing date will be 21 days from the appearance of this notice.



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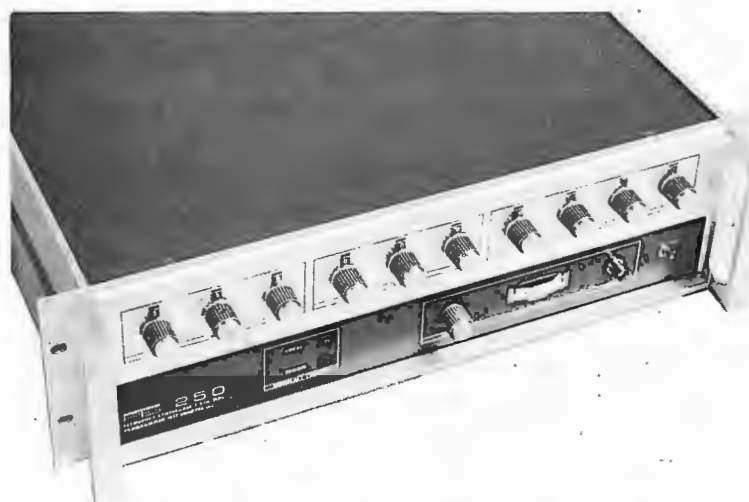
## PTS 500

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Resolution: 0.1Hz-100KHz (opt.)  
Switching: 5-20 $\mu$ s  
Output: +3 to +13dBm: 50 ohm  
Spurious Outputs: -70dB

Phase Noise: -63dBc, (0-15KHz)  
Freq. St'd: Oven, TCXO, Ext.  
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June 30, 1987

(Received 7 July 1987)

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

Title: Quantitation of Carbon Types Using the DEPT/QUAT NMR Pulse Sequences

Dear Barry,

A practical procedure was developed whereby the fraction of carbon types ( $^{13}\text{CH}_n$ ,  $n = 0-3$ ) in fossil fuel-derived oils can be quantitatively determined using the pulse sequences DEPT<sup>1</sup> (Distortionless Enhancement by Polarization Transfer) and QUAT<sup>2</sup> (Quaternary-Only Carbon Spectra). Because these two techniques differ in the mechanism for signal enhancement, the NMR data are not directly related. A previously described method in the literature<sup>1</sup> used to compensate for the missetting or field inhomogeneity of the  $^1\text{H}$  pulse and to provide qualitatively good edited spectra can also be used to obtain quantitative carbon-type analysis. The methodology described is shown to be useful not only for pure compounds and simple mixtures but also for the analysis of complex mixtures such as fossil fuel-derived products. The DEPT/QUAT technique is preferred over most quantitative spin-echo experiments because the time necessary for data acquisition and reduction is much less.

Carbon type subspectra were obtained from the addition and subtraction of the initial DEPT spectra. Although the DEPT method provides quantitative data for methyl, methylene and methine carbons, it does not provide any quantitative data on the quaternary carbons. The integrated edited DEPT spectra for the three carbon types cannot be compared to the integrated quaternary-only carbon spectrum because the methods to obtain the spectra differ in signal enhancement efficiencies. It is possible, however, to relate quantitatively through equation 1 the integrated spectra obtained by the two techniques to obtain a complete quantitative carbon type analysis.

$$\sum I_{\text{CH}_n} = k I [\text{N} - \text{QUAT}] \quad (1)$$

where  $\sum I_{\text{CH}_n}$  is the sum of the integrated values of the carbon types obtained from the DEPT subspectra and  $I [\text{N} - \text{QUAT}]$  is the integrated value from the spectrum obtained from the computer subtraction of the quaternary-only carbon spectra from the  $^{13}\text{C}$  normal spectrum. All integration values were referenced to the integration value of the normal  $^{13}\text{C}$  spectrum taking into account the differences in gain settings between spectra.



Equation 1 is solved for the proportionality constant  $k$ . Once  $k$  has been determined, the fraction of carbon types  $f_n^C$ , in a sample can be determined using equations 2 through 4.

$$kI^{\ominus}_{\text{QUAT}} = kI^{\ominus}_C \quad (2)$$

$$kI^{\ominus}_C + I^{\ominus}_{\text{CH}} + I^{\ominus}_{\text{CH}_2} + I^{\ominus}_{\text{CH}_3} = I^{\ominus}_{\text{Total}} \quad (3)$$

$$f_n^C = \frac{I^{\ominus}_n}{I^{\ominus}_{\text{Total}}} \quad (4)$$

where  $I^{\ominus}_n$  is the integrated value from the specific carbon type spectrum.

Table I gives the carbon and hydrogen-type distribution for a western shale oil using the above method. The hydrogen-type distribution was calculated from the  $^{13}\text{C}$  DEPT/QUAT data. Table II lists several average structural parameters for the western shale oil calculated from the DEPT/QUAT data and determined directly from  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data. Also given is the atomic H/C ratio calculated from elemental analysis and  $^{13}\text{C}$  DEPT/QUAT spectral analysis. The data by the different techniques is in good agreement.

Table I. Carbon and Hydrogen-Type Distributions for a Western Shale Oil<sup>1</sup>


Carbon-Type	Western Shale Oil	
	C (atom-%)	H (atom-%)
C		
Aromatic	14.8	
Olefinic	0.0	
Aliphatic	0.3	
CH		
Aromatic	7.6	4.4
Olefinic	1.0	0.6
Aliphatic	2.5	1.4
CH <sub>2</sub>		
Olefinic	1.6	1.9
Aliphatic	57.9	66.7
CH <sub>3</sub>		
Aromatic and Aliphatic	14.5	25.1

<sup>1</sup> From the Material Balance Fischer Assay of Green River oil shale

Table II. Average Structural Parameters for a Western Shale Oil

Structural Parameter	Western Shale Oil (MBFA)
Atomic H/C	
Combustion	1.76
NMR ( $^{13}\text{C}$ -DEPT)	1.73
Hydrogen, Aromatic (%)	
NMR ( $^1\text{H}$ -Direct)	4.3
NMR ( $^{13}\text{C}$ -DEPT)	4.4
Hydrogen, Olefinic (%)	
NMR ( $^1\text{H}$ -Direct)	2.9
NMR ( $^{13}\text{C}$ -DEPT)	2.4
Hydrogen, Aliphatic (%)	
NMR ( $^1\text{H}$ -Direct)	92.8
NMR ( $^{13}\text{C}$ -DEPT)	93.2
Carbon Aromatic (%)	
NMR ( $^{13}\text{C}$ -Direct)	23.6
NMR ( $^{13}\text{C}$ -DEPT)	24.9
Carbon Olefinic (%)	
NMR ( $^{13}\text{C}$ -Direct)	2.6
NMR ( $^{13}\text{C}$ -DEPT)	2.6
Carbon Aliphatic (%)	
NMR ( $^{13}\text{C}$ -Direct)	76.4
NMR ( $^{13}\text{C}$ -DEPT)	75.2

Sincerely,

  
Daniel A. Netzel

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2. Bendall, M. R., D. T. Pegg, D. M. Doddrell, S. R. Johns, and R. I. Willing. J. Chem. Soc., Chem. Commun., 1982, 1138.

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Personal No.



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OX1 3QZ

Professor Bernard L. Shapiro,  
Department of Chemistry,  
Texas A and M University,  
College Station,  
Texas 77843-3255,  
U.S.A.

23rd June, 1987.  
(Received 30 June 1987)

Dear Barry,

Hogwash/Maximum Entropy/Change of Address

We have been examining non-linear techniques for resolution enhancement, following the current trend to off-line data processing. It is well known that the maximum entropy algorithm can be used for resolution enhancement simply by introducing a sensitivity enhancement weighting of the free induction decays derived from the trial spectra (1, 2). Alternatively we could use "HOGWASH", a program based on a data processing technique used in radioastronomy (3, 4). The idea behind HOGWASH is very simple - we subtract a small proportion of the tallest peak in the spectrum at each stage of the iteration, building up a table of coordinates and intensities of each peak located in this manner. When a weak line overlaps an intense line there is an appreciable displacement of its apparent frequency; subtraction of the taller peak counteracts this displacement. At the end of the iteration the spectrum is reconstructed using a narrow linewidth.

Our idea was to apply both the maximum entropy method and HOGWASH to the same high resolution spectrum in order to study the relative effectiveness of the two techniques for resolution enhancement. Both techniques used a line shape function derived experimentally. Our conclusions (5) were that both methods achieved an enhancement approaching a factor of about six. Both depended on the proper choice of operating parameters; when a poor choice was made the spectra contained spurious lines. Owing to the non-linearity of the operation, the small splittings observed by maximum entropy or HOGWASH differed slightly from those extracted by linear deconvolution methods. Within these limitations, there was little to choose between the two rival techniques except that HOGWASH used less data storage (roughly one-sixth) and ran faster (roughly twenty times) than the maximum entropy program. A full comparison has been written up and submitted for publication (5).

Finally I would like to record my change of address, effective 1st July 1987.

Department of Physical Chemistry,  
Lensfield Road,  
Cambridge CB2 1EP. (England).

Kindest regards,

*Ray*

Ray Freeman

- 1) E.D. Laue, M.R. Mayger, J. Skilling and J. Staunton, J. Magn. Reson. 68, 14 (1986).
- 2) S.F. Gull and G.J. Daniell, Nature (London) 272, 686 (1978).
- 3) J.A. Hogböm, Astron. Astrophys. Suppl. 15, 417 (1974).
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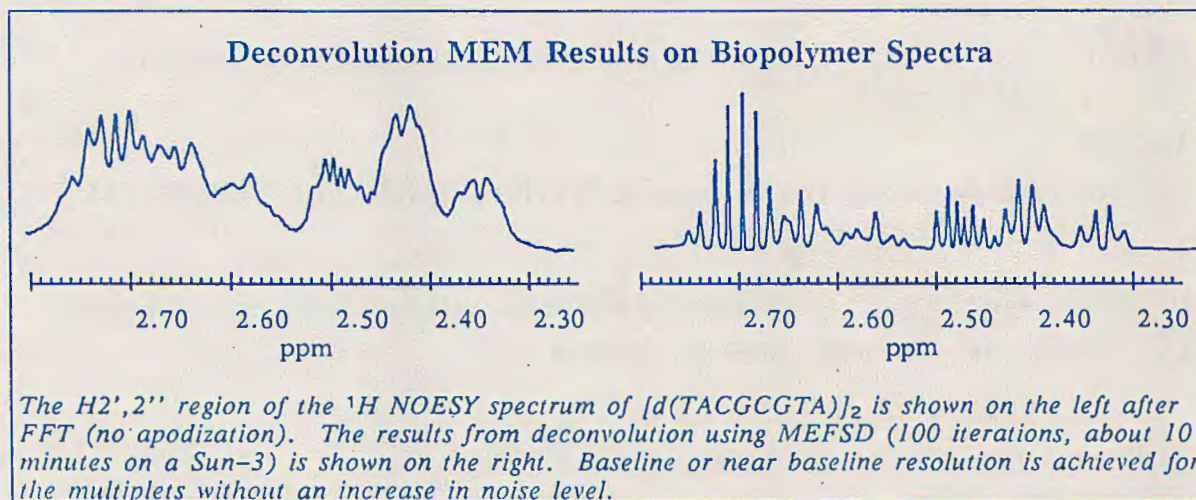
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**TOWSON STATE UNIVERSITY**  
**COLLEGE OF NATURAL AND MATHEMATICAL SCIENCES**  
**TOWSON, MARYLAND 21204**

July 20, 1987

Department of Chemistry

(Received 29 July 1987)

(301) 321-3058

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

Dear Barry:

"News from the Academic Trenches"

TSU has no graduate programs in Physics or Chemistry and only a very small undergraduate or faculty research effort (thanks to a 12 hour per week teaching load). We teach (and grade) all of our own labs - good for the students, hard on us. However, we are reasonably well equipped and committed to having every piece of equipment used in undergraduate courses, and that includes our NMR's. We recently saved our Perkin-Elmer R-12 by acquiring a similar instrument from Johns Hopkins for parts; the extra magnet is now part of a Gouy balance. Our current pride and joy is our 4-year old multinuclear JEOL FX-90Q. The floppy disc drive lasted less than three years, was repaired once, hobbles along and is being replaced by a better floppy drive using some of the Dean's money. We acquired an old VT unit from Cal Tech. We just added a Ballston air dryer so we could use the VT unit; the compressor supplied with the 90Q produced too little air.

Students in Instrumental Analysis use the FX-90Q for organic unknowns; the time and damage is minimized if the students come in groups with their samples and are supervised the whole time. With my intro organic class, I ran the samples for them while they watched; they have used the R-12 in the past. Next I'd like to see the instrument used to teach Fourier techniques and in Inorganic Lab. It's a tough compromise - there is no point in having an instrument if it isn't used, but undergraduates tend to be hard on equipment. Our experience shows it is possible to use these instruments effectively in undergraduate courses, but it requires a commitment of people to teach and supervise. I promise a more technical contribution next time from our undergraduate research program.

Yours sincerely,



Linda M. Sweeting



Barry Shapiro  
TAMU NMR Newsletter, Texas A & M University  
College Station, Texas 77843

July 20, 1987  
(Received 29 July 1987)

### NMR1 Software

Dear Barry:

Recently TAMU/NMR published a letter with some complimentary and several negative comments on NMR1, our 1-D NMR software data reduction and analysis program. In this letter we would like to respond to the criticisms, some quite fair, of NMR1.

The first comment that we must make is that in early 1987, our company recognized the need for a considerable increase in customer support and response to customer requests. We now have two staff members whose primary function is to respond rapidly to customer needs. The letter to TAMU NMR was from a customer not currently under software support and using a version of NMR1 that is out of date. Version 3.8 of NMR1, released earlier this month, has a number of major enhancements and "bug fixes". We still recognize areas of need and our company is committed to continue development of the finest data reduction and analysis software for NMR spectroscopy.

Major enhancements for Release 3.8 of NMR1 and Release 1.5 of MEM/LPM include:

1. New autophasing and interactive phasing that is convenient and fast.
2. A new auto command (AU) exists that fully processes NMR data, asking users only a few questions. New AU options will follow.
3. Our excellent automatic curve fitting module has been expanded, with expanded documentation.
4. Several "Bugs" that occurred with occasional spectra, in integration and peak analysis, have been fixed.
5. MXQET, a solid state lineshape analysis program written by Bob Vold, et al, has been adapted to NMR1 and a new input editor was created to ease data entry.
6. MEM processing has been advanced to incorporate deconvolution MEM processing of spectral segments selected by the user from large data sets, even those with very small peaks in the presence of large solvent lines.
7. Linear prediction processing is now supported, incorporating a high quality user interface.
8. Addition of new apodization functions such as TRAF apodization.
9. In the next release, user modules will be supported in NMR1 via 9 user commands and fully documented instructions for implementation of those routines.
10. The Release 3.8 NMR1 Manual (in preparation, to be distributed next month -- release update notes are now available for users) is greatly expanded and will have a full index. The manual is now replete with graphics and sample session information.

There are still problems in polymer analysis, which is "in the shop", and will be re-released at Revision 4.0.

We have, in fact, corrected some internal problems left over from the days of student programmers. NMR1 is now under the total control of a professional staff.

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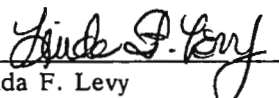
NMRi is not resting on its laurels; indeed we know we need to advance our software and keep it at the state-of-the-art. We value user input about our programs and now we have the people to ensure that customers get rapid response to their questions or problems. Subscribers should call our 800 phone number for help; others - please call or write to us.

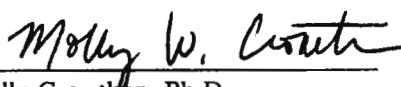
Spectroscopists who came to ENC and the International Conference on NMR Spectroscopy in Canterbury, England, got to see NMR1 and NMR2, and MEM/LPM running on our **SpecStation™** systems. We believe these demonstrations showed that our software is extremely powerful and also reliable. We invite criticism (and compliments) and will respond as a team to future needs.

In the next major releases of **LAB ONE™** software, expect new application of MEM and linear prediction techniques, further automation of complex command sequences, and other enhancements. Soon to follow will be advanced pattern recognition programs, tools for 3-D structure determination and advanced image enhancement features.

Yours sincerely,

NEW METHODS RESEARCH, INC.

  
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 Manager of Marketing and  
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Professor B. L. Shapiro,  
 Department of Chemistry,  
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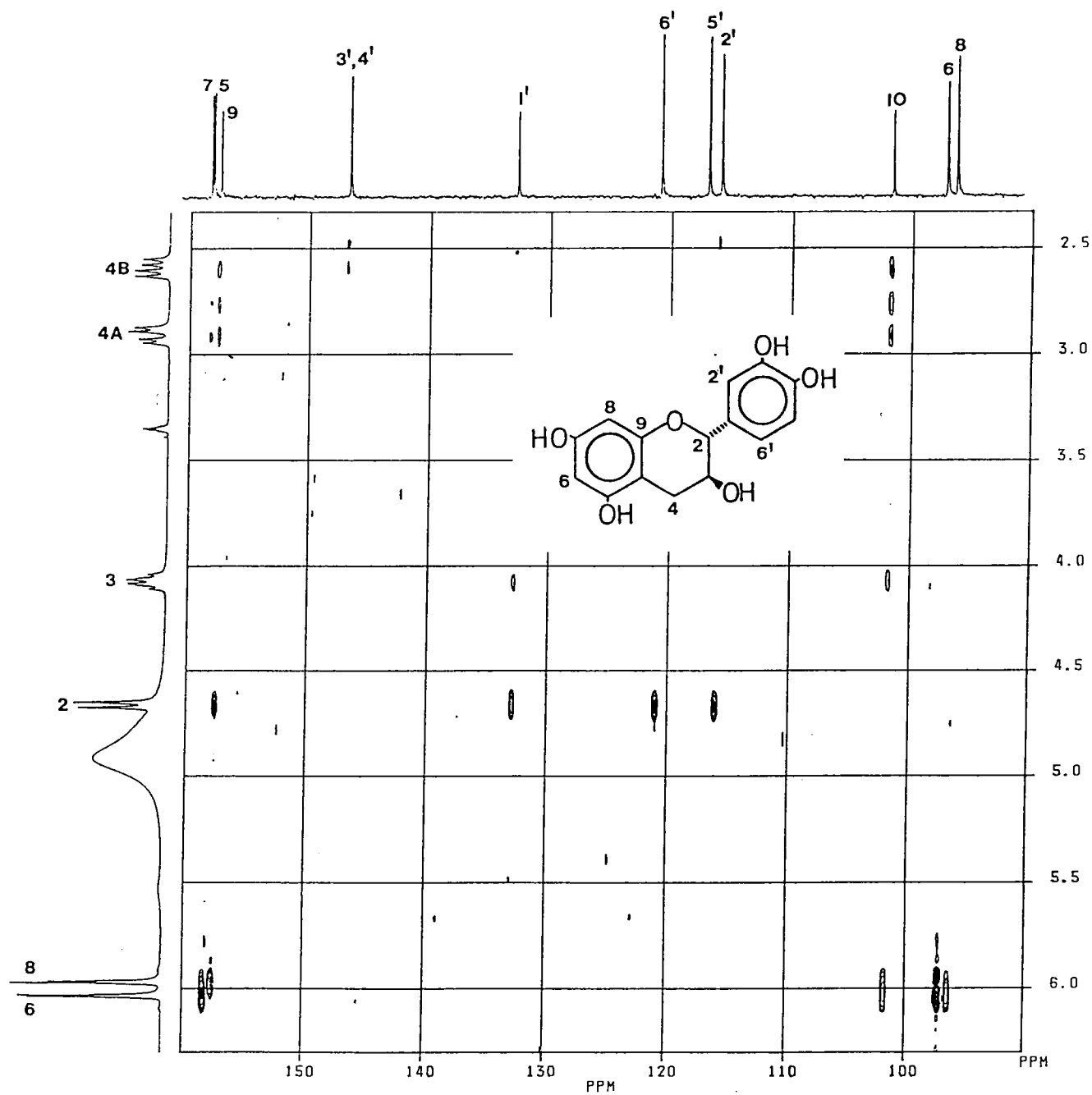
Unambiguous assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  spectra of catechin

Dear Professor Shapiro,

Recently we have been collaborating with Professor Strack of the University of Cologne on a project concerned with the effects of pollution ("acid rain") on pine trees. During the investigation of the phenolics in pine needles it was necessary to assign the  $^1\text{H}$  and  $^{13}\text{C}$  spectra of (+)-catechin. Although this trivial compound has been investigated previously ambiguities concerning the assignment of H-6, H-8, C-6 and C-8 exist. A similar problem has recently been solved for the flavone apigenin by De Bruyn et al. (Magn.Res.Chem. 1986, 24, 879), who took extensive  $^{13}\text{C}$  spectra with selective  $^1\text{H}$  irradiation. It occurred to us that a more general solution to such problems would be to take long-range 2D  $^{13}\text{C}$ - $^1\text{H}$  shift correlated spectra. For catechin the normal 2D  $^{13}\text{C}$ - $^1\text{H}$  shift correlated spectrum allowed unambiguous assignments of the hydrogen bearing carbons, apart from C-6 and C-8. The corresponding COLOC spectrum (figure), and the reasonable assumption that  $^2\text{J}(\text{CH})$ ,  $^3\text{J}(\text{CH}) > ^4\text{J}(\text{CH})$ , allowed not only the assignment of all the quaternary carbons but also the unambiguous assignment of both the  $^1\text{H}$  and  $^{13}\text{C}$  shifts of 6 and 8. H-8 shows a long-range correlation with C-7, C-9, C-10 and C-6, while H-6 correlates with C-7, C-5, C-10 and C-8.

Yours sincerely,

*Victor Wray*  
 (Dr.) Victor Wray



Contour plot of the 2D COLOC  $^{13}\text{C}$  NMR spectrum of catechin in  $\text{CD}_3\text{OD}$ .



UNIVERSITY OF MISSOURI-COLUMBIA

College of Arts and Science

Department of Chemistry

123 Chemistry Building  
Columbia, Missouri 65211  
Telephone (314) 882-2439

July 20, 1987

(Received 27 July 1987)

Professor Bernard Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas 77843Determination of  $^{13}\text{C}$  CSA from  
Differential Line Broadening

Dear Dr. Shapiro:

Recently there have been a number of studies of differential line broadening (DLB) in coupled spin systems. The effect is attributed to the interference term between the dipole-dipole (DD) and chemical shift anisotropy (CSA) relaxation mechanisms. Such effect is likely to be observed when (1)

1. the motion of system is not in the extreme narrowing limit.
2. the CSA and DD terms are of comparable magnitude.

We have observed, DLB on  $^1\text{H}$  coupled methyl  $^{13}\text{C}$  multiplet in a viscoelastic micellar solution (Fig.). Similarly effect was observed in methyl  $^{13}\text{C}$ -enriched tRNA(2). We have derived DLB for systems where there is slow reorientational motion and fast internal motion by solving the stochastic Liouville equation. The  $m_s$  (proton spin state)-dependent  $T_2$  is given by

$$\frac{1}{T_2} = a + bm_s + cm_s^2$$

where the  $b$  term arises from the interference between DD and CSA and the  $c$  term arises from DD and is important when  $\tau_c$  is slow. Therefore, from the linewidth differences in a methyl multiplet, both the slow correlation time and the  $^{13}\text{C}$  CSA can be determined. In this case the CSA of N-methyl  $^{13}\text{C}$ , which has not been measured before, was determined.

The knowledge of the slow correlation time and the order parameter for the methyl reorientation from  $^{13}\text{C}$   $T_1$  and NOE at one magnetic field according to the models of Wennerstrom et al. and Lipari et al. (3) (see Table).

This technique should have good potential in the study of molecular dynamics of macromolecules and molecular aggregates.

Sincerely yours,

*Lian-Pin Hwang*  
Lian-Pin Hwang  
Professor of Chemistry  
National Taiwan University

*Tuck C. Wong*  
Tuck C. Wong  
Associate Professor  
of Chemistry

TCW/sdl

(continued on page 21)



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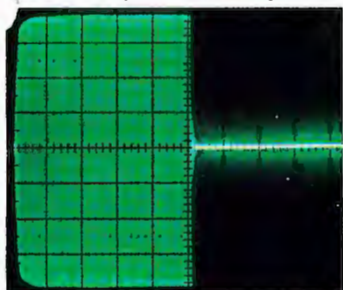
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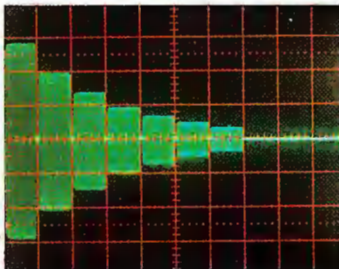
A 5 $\mu$ sec  $^1\text{H}$  observe pulse. ▽



15° phase shift through 360°. ▸

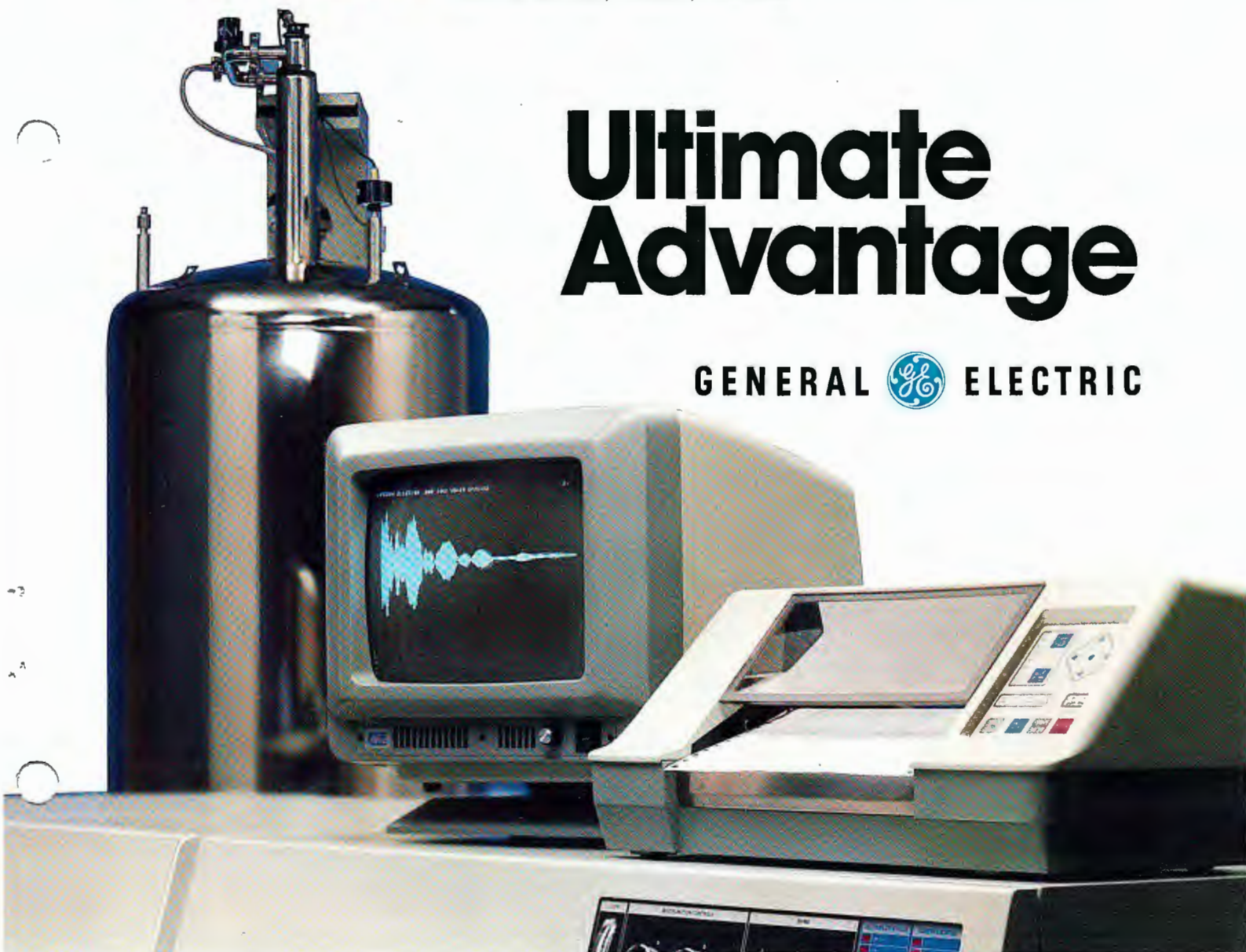


Shaped decoupler pulse. ▸



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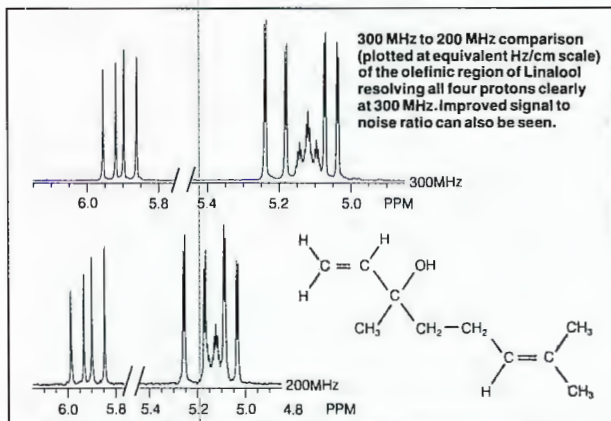
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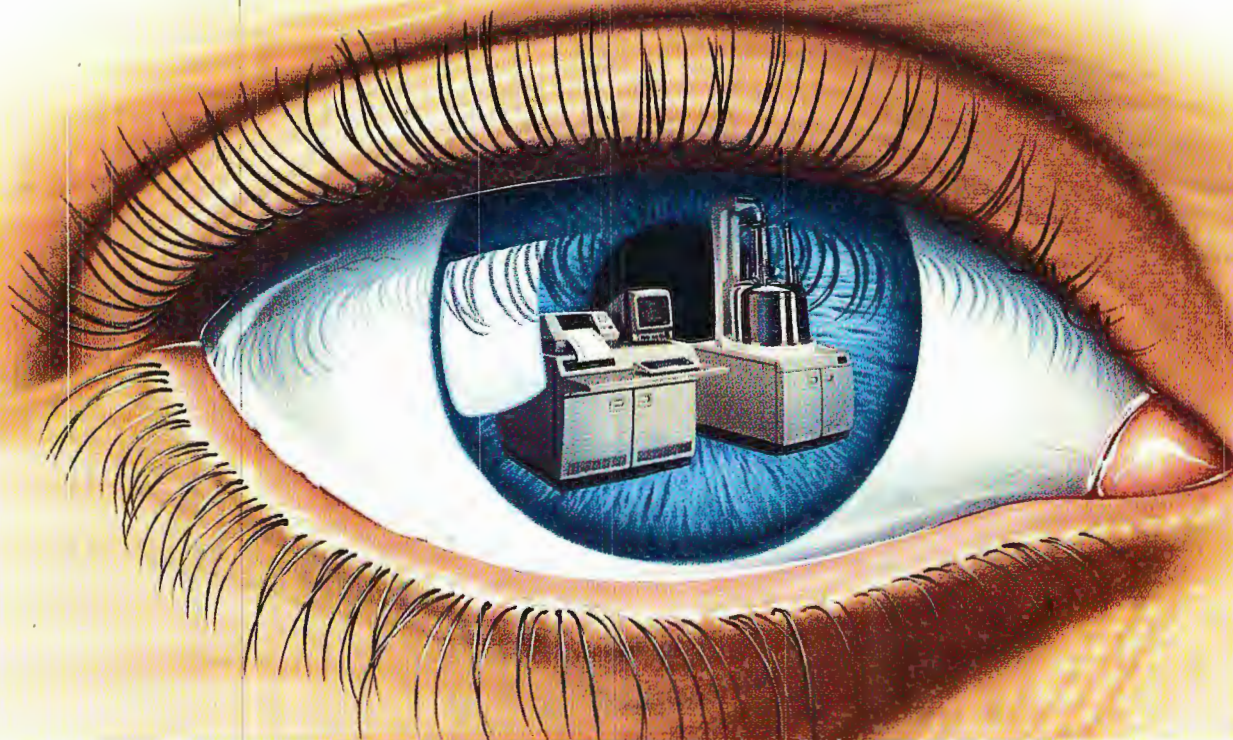
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2. Gracz, H (private communication).
3. Wennerstrom, H., et al. J. Am. Chem. Soc. 1979, 101, 6860.  
Lipari, G., et al. J. Am. Chem. Soc. 1982, 104, 4546.

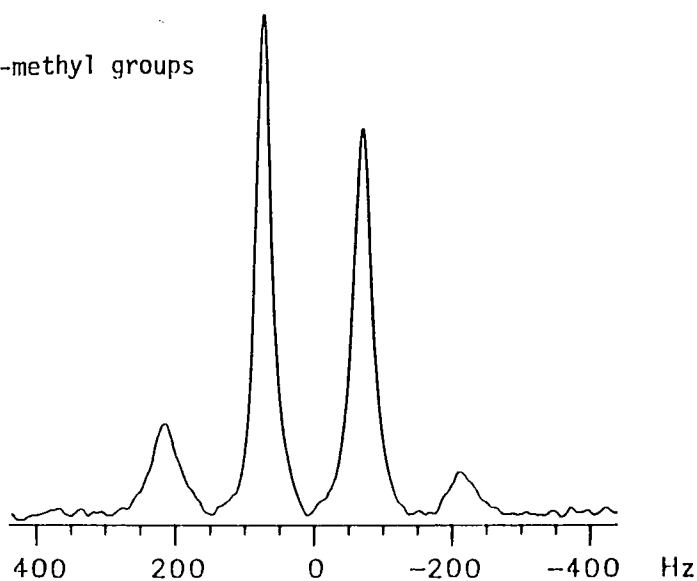
Table 1. The correlation time for aggregate reorientation and CSA (for N-methyl  $^{13}\text{C}$ ) in a CTAB-sodium salicylate (15 mM) viscoelastic micelle from DLB.

Temp(°C)	$\Delta\nu(-\frac{1}{2}, \frac{1}{2})$ (Hz) <sup>a</sup>	$\Delta\nu(3/2, \frac{1}{2})$ (Hz)	$\tau_c^s (10^{-8}\text{s})$	$\Delta\sigma(\text{ppm})$
38	10.0±2.5			
42	7.5±1.0	21.1±3.0	2.3±0.5	-82±20
47	6.0±0.8	20.4±2.0	2.2±0.4	-80±12
52	4.6±0.5	18.5±1.5	2.0±0.25	-62±7
56	4.0±0.3	15.0±1.0	1.6±0.15	-62±6

Table 2. Correlation times and the order parameter from DLB and multifield  $^{13}\text{C}$   $T_1$  and NOE.

Temp(°C)	7.0 T		9.4 T		$\tau_c^s (10^{-8}\text{s})$	$\tau_c^f (10^{-11}\text{s})$	$S$
	$T_1$	$1+\eta$	$T_1$	$1+\eta$			
42	0.619	2.270	0.753	2.517	2.3	1.79	0.389
47	0.721	2.382	0.841	2.604	2.2	1.62	0.322
52	0.802	2.465	0.915	2.687	2.0	1.50	0.268

Fig. DLB in the N-methyl groups in CTAB





**ABBOTT**

Abbott Laboratories  
Abbott Park, Illinois 60064

June 22, 1987  
(Received 13 July 1987)

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

#### Data Processing on a VAX Network

Dear Dr. Shapiro:

In recent years more and more large NMR facilities have been interfacing their spectrometers to an external computer network. The advantages of such an approach are well known and broadly recognized. The major drawback for such networking is the lack of adequate available software.

Most of the software used on the Abbott NMR VAX was developed in-house. Using this software, large numbers of one- and two-dimensional spectra are routinely transferred from Nicolet/GE spectrometers to the VAX via serial lines, assigned reference numbers, entered into a laboratory database (ORACLE, Oracle Corp., Belmont, CA) and archived onto magnetic tape (ARCHIVER, Strategic Information, Burlington, MA). The data files are then converted to the file format appropriate to the processing program to be used.

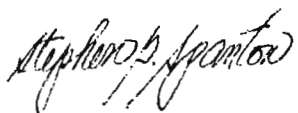
Two-dimensional data files are transformed and plotted using a version of FTNMR (D. Hare) which has been extensively modified at Abbott, principally by Dr. Erik Zuiderweg. One-dimensional spectra are processed using one of two programs, BATCHFT and ABNMR, both developed in this laboratory.

BATCHFT, as the name implies, is a program for the processing of routine  $^1\text{H}$  spectra in batch mode. Acquisition of such spectra has been

automated using a General Electric QE-300 with a sample changer. Unfortunately, since GE spectrometers do not have plot queues, spectra plotted as part of an automated queue delay the data acquisition of the following samples. Worse still, an overnight plotter error stops the entire queue. By moving the data processing to the VAX, we have obviated these problems, resulting in significantly higher sample throughput and spectrometer reliability. The integration routine of BATCHFT searches the spectrum for regions of baseline in which to zero the integral. In addition, the program plots a vertical expansion of the spectrum using a variable scale factor that it determines automatically.

ABNMR is our program for the interactive processing of one-dimensional spectra. It is intended for use on serial port graphics terminals. The FORTRAN code contains generic graphics calls provided by the graphics package TEMPLATE (Megatek Corp., San Diego, CA), making the program largely device independent. This allows us with a minimum of effort to support virtually any graphics terminal which is supported by TEMPLATE. ABNMR provides us with virtually all of the capabilities for processing one-dimensional spectra which are present in spectrometer software. In addition, it contains a routine for reading data files in the format of FTNMR.

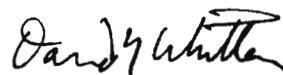
Please credit this contribution to the subscription of Ms. Ruth Stanaszek.



Stephen G. Spanton



Richard L. Stephens



David N. Whittern



# THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P.O. BOX 398707, CINCINNATI, OHIO 45239-8707

June 29, 1987

(Received 13 July 1987)

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

## Solid-State $^{13}\text{C}$ NMR of Amine/Carboxylic Acid Complexes

Dear Professor Shapiro:

We have been using solid-state  $^{13}\text{C}$  NMR to determine the stoichiometry and phase properties of tertiary amine/carboxylic acid complexes. As an example, figure 1 shows the CPMAS  $^{13}\text{C}$  NMR spectra of solid 1:2 (1a) and 1:3 (1b) mixtures of a dimethylalkyl amine (DMAA) and a long chain fatty acid (FA) obtained on our Bruker CXP-300 spectrometer, with a 7 mm Doty probe. The results, along with information obtained by DSC and x-ray diffraction, indicate the presence of  $\text{AB}_2$  (figure 1a) and  $\text{AB}_3$  (figure 1b) complexes, where A = DMAA and B = fatty acid.<sup>2</sup> In particular, figure 1a exhibits two carboxyl resonances of equal intensities at  $\delta = 173.7$  and  $178.0$  ppm. Note that the two N-methyl carbons are inequivalent ( $\Delta\delta = 2.5$  ppm) in the  $\text{AB}_2$  complex. Figure 1b shows three carboxyl resonances, as expected for an  $\text{AB}_3$  complex. In this case, the chemical shift inequivalence of the two  $-\text{NCH}_3$  carbons is 3.4 ppm.

To confirm the above results,  $^{13}\text{C}$  NMR spectra were obtained for a series of DMAA:FA solid mixtures. Figure 2 shows the carboxyl, N-methyl and N-methylene regions of the spectra, on an expanded scale. The pattern of resonances for the  $\text{AB}_2$  complex (2c) consistently appears in the spectra of 1:<2 molar ratio mixtures (figure 2c  $\rightarrow$  2a). Two additional resonances with increasing intensities appear at  $\delta \sim 45$  and  $58$  ppm due to the excess DMAA, as the ratio of tertiary amine to fatty acid increases. On the other hand, the spectra of 1:>3 mixtures consist of resonances due to the  $\text{AB}_3$  complex (2d), and an additional peak at  $181$  ppm due to the excess fatty acid (FA).

Variable temperature studies, using a sealed Pyrex MAS rotor insert<sup>1</sup> and the pulse sequence for the simultaneous observation of solid and liquid components,<sup>2</sup> are currently underway to establish the phase properties of this binary system.

Sincerely,

THE PROCTER & GAMBLE COMPANY  
Research and Development Department

*Charles D. Sazavsky*  
Charles D. Sazavsky

*Fouad S. Ezra*  
Fouad S. Ezra

<sup>1</sup> P. J. Giammatteo, et al, J. Mag. Res. 71, 147-150 (1987).

<sup>2</sup> W. L. Earl and D. L. Vanderhart, J. Mag. Res. 48, 35-54 (1982).



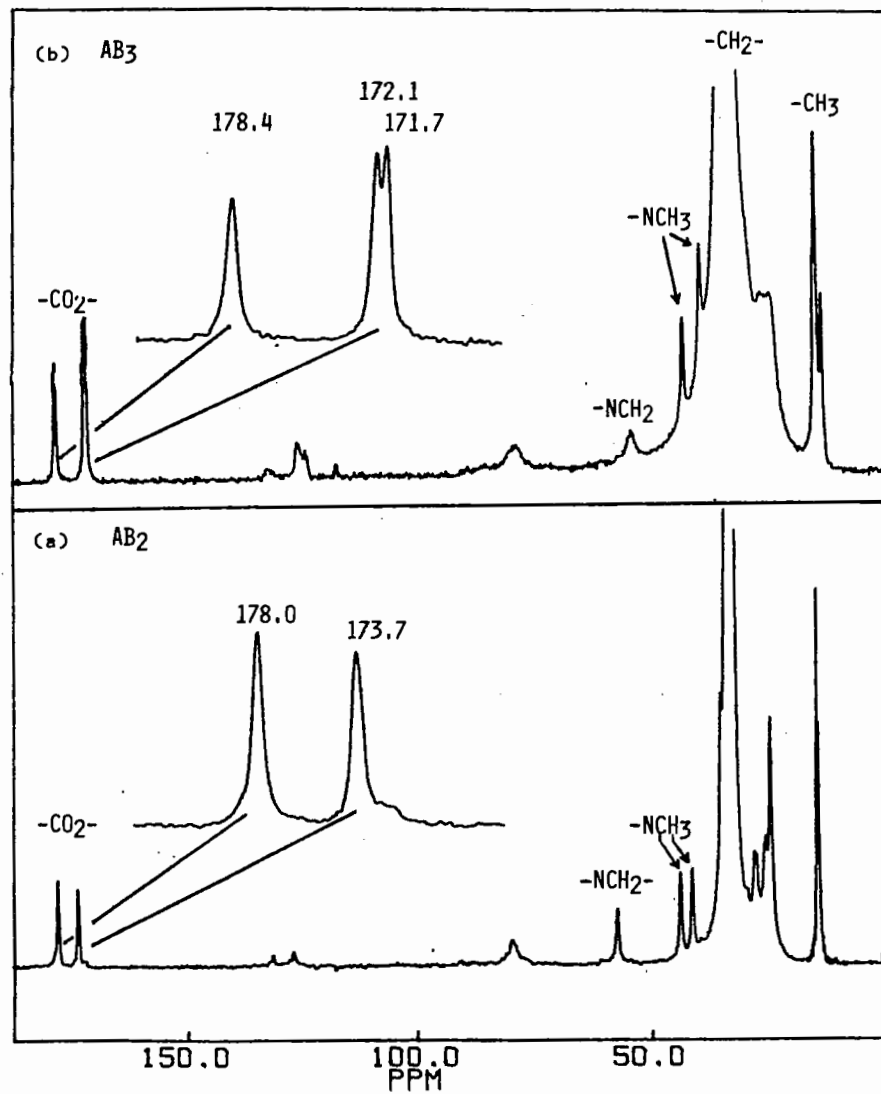


FIGURE 1

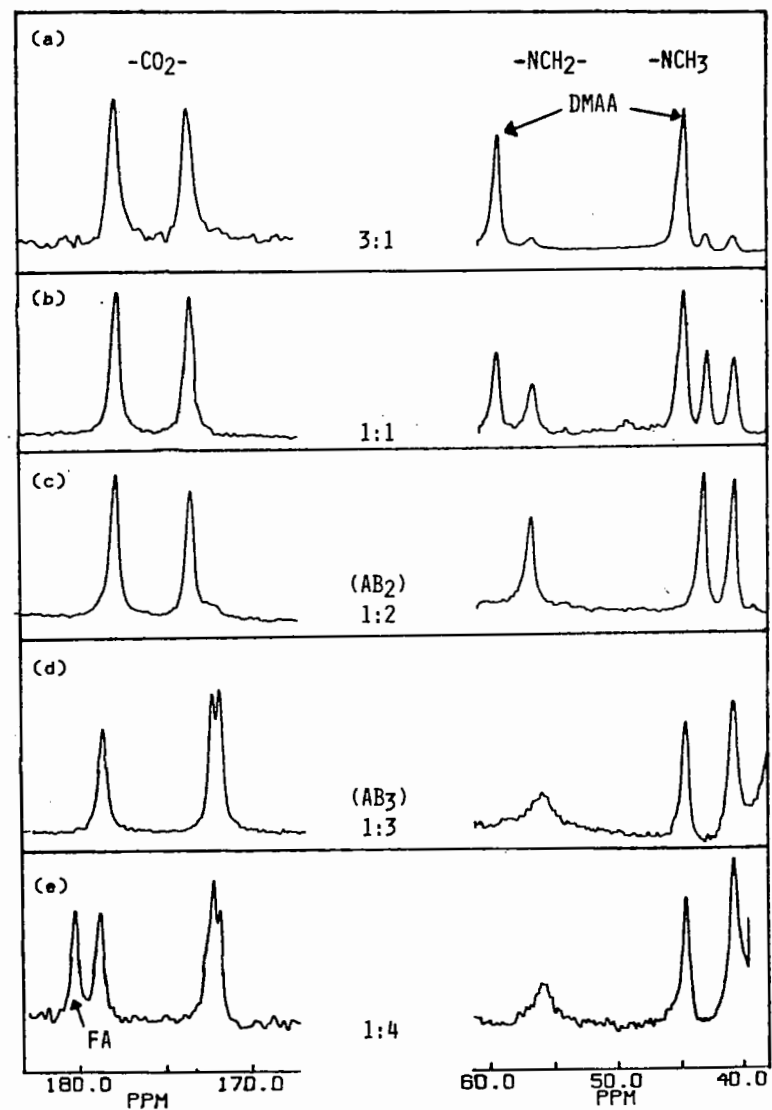


FIGURE 2



# THE UNIVERSITY OF SYDNEY

## DEPARTMENT OF BIOCHEMISTRY

SYDNEY N.S.W. 2006  
AUSTRALIA

TELEPHONE: (02) 692-2222  
TELEX: UNISYD 26169

30 June 1987  
(Received 13 July 1987)

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

### Performance of a Probe Modified for Field Gradient Studies

Dear Barry,

Probe modifications in the vicinity of the coils are generally considered to have deleterious effects on performance for obtaining high resolution spectra. Our recent experience with incorporating a field gradient coil on a broadband probe for our widebore XL-400 suggests that this need not necessarily be the case.

As part of a study of molecular diffusion, we initially sought to introduce a gradient via a standard homospoil pulse, but found that there was insufficient attenuation of a spin-echo spectrum using the gradient pulse lengths we wanted, even after increasing the gradient strength by a factor of five with a minor modification to the Oxford shim power supply.

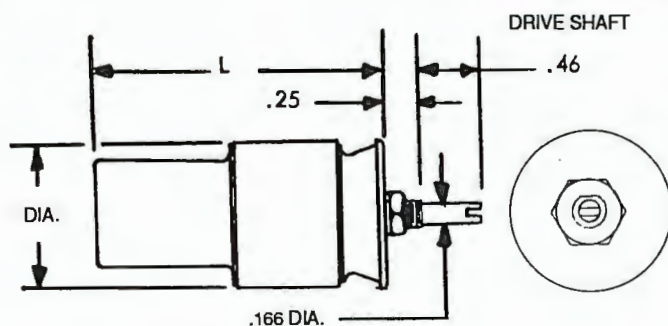
The gradient experienced by the sample was significantly increased by applying a pulse from an external power supply to a coil mounted outside the decoupler coil of the probe. Various coil geometries were studied but all coils were wound on Perspex formers and embedded in epoxy resin, and the former was secured to the decoupler coil insert with nylon thumbscrews. Connections to the power supply were taken through the conduit normally used for rods containing low frequency tuning capacitors. Interference with the temperature control circuitry was circumvented by appropriate shielding of connections to the probe base. The configuration described allowed coils to be interchanged relatively easily.

Resolution and sensitivity were checked routinely for  $^{13}\text{C}$  observation and found to easily meet specifications (ASTM sample). Performance with a 10-turn coil, which gave gradients of  $\sim 20 \text{ Gcm}^{-1}$  in our system, was as follows: resolution, 0.16 Hz (specification  $\leq 0.2 \text{ Hz}$ ); lineshape, 3.7 Hz at 0.55% ( $\leq 4 \text{ Hz}$ ), 7.9 Hz at 0.11% ( $\leq 10 \text{ Hz}$ ); spinning side bands, 0.5% ( $\leq 1\%$ ); observe  $90^\circ$  pulse width, 24  $\mu\text{sec}$  ( $\leq 25 \mu\text{sec}$ ); sensitivity, 419:1 (400:1).

(continued on page 29)

# Polyflon DESIGN DATA

## RF Variable Capacitors (0.8-85pF) Non-Magnetic - High Voltage - High Power - High Q Screwdriver Adjust Non-Rotating Piston Series



### Specifications

Capacitance Range	0.8-85pF
Working Voltage	To 10 Kv
Dielectric Strength	200% of working voltage
Quality Factor (Q)	5000 or greater
Insulation Resistance	10 <sup>16</sup> Megohms
Operating Temperature	-55°C to 150°C
Temperature Coefficient	50 ppm/°C
Tuning Torque	4 inch ounces (max)

### Design

PTFE anode and mount surfaces are metalized with electro-deposited copper. Polyflon's proprietary plating process eliminates the possibility of air being trapped between the PTFE and copper interface which could break down under voltage stress.

### Notes

1. Working volts and maximum RMS current must not occur simultaneously.
2. Peak test voltage rating may be used for pulsed voltage applications. Peak pulsed current will be limited by the duty cycle that will provide an average current that does not exceed the maximum RMS current.
3. Mounting dimension: 1/4" diameter "D" hole. Hardware: 1/4-32 hex nut and internal tooth lockwasher. Mounting flange is at the bottom of the capacitor.

### Ordering Instructions

<b>NRP-VC</b>	<b>10-</b>	<b>12-</b>	<b>26</b>	<b>A</b>
Style	Kv(peak) test			Lead Option
	Max. capacitance rating expressed in picofarads (pF).			Drive shaft option (see table).

Part Number	Capacitance Range (pF)	Peak (Kv) Working Volts	Peak (Kv) Test Volts	Max. (RMS) Current (amps)	Dimensions/inch (mm)		Wt./Ounces (Approx)
					L(±.020")	Dia.(±.020")	
NRP-VC5-10-*	0.8-5	5	10	2.30	1.560 (39.6)	0.500 (12.7)	0.40
NRP-VC10-12-*	0.8-10	6	12	3.60	1.830 (46.5)	0.625 (15.9)	0.80
NRP-VC25-6-*	5-25	3	6	5.70	1.620 (41.1)	0.910 (23.1)	1.25
NRP-VC25-6B-*	5-25	3	6	4.20	1.620 (41.1)	0.625 (15.9)	1.25
NRP-VC25-15-*	5-25	10	15	7.20	1.770 (45.0)	1.125 (28.6)	2.00
NRP-VC30-6-*	3-30	3	6	10.00	2.250 (57.2)	1.500 (38.1)	4.00
NRP-VC50-6-*	5-50	3	6	12.50	2.250 (57.2)	1.500 (38.1)	3.50
NRP-VC70-15-*	3-70	10	15	20.00	3.250 (82.6)	1.625 (41.3)	4.50
NRP-VC85-6-*	5-85	3	6	20.00	3.250 (82.6)	1.500 (38.1)	4.10

\*Add code number for leads. See lead code number table below.

### Drive Shaft Option Table

Option	Description
A	Extension Shaft: .125" dia. x 3" long delrin rod with .500" dia. x .250" thick knurled delrin knob.
B	Coupling Adapter: .375 O.D. x .170 I.D. (female) x .500" long to .250" dia. (male). Overall length is 1". (Has set screws)
C	Coupling Adapter: .437" O.D. x .170" I.D. (female) to .250" dia. (female) overall length is 1". (Has set screws)

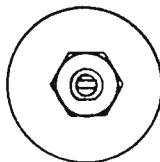
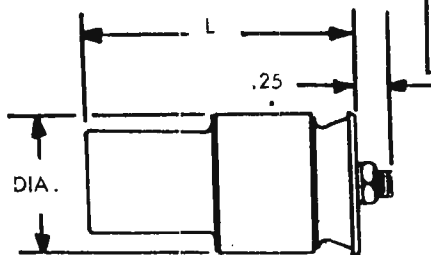
### Lead Option Table

06	without lead wires
16	3" wire, top only - in line with flat
26	3" wire, top and bottom - in line with flat
36	1-1/2" strap, top only - in line with flat
66	3" wire, top only, opposite flat
76	3" wire, top and bottom - opposite flat
86	1-1/2" strap, top only - opposite flat

# Polyflon DESIGN DATA

## RF Variable Capacitors (0.3-25pF)

**Non-Magnetic - High Voltage - High Power - High Q**  
Screwdriver Adjust Rotating Piston Series



### Specifications

Capacitance Range	0.3-25pF
Working Voltage	To 10 Kv Peak
Dielectric Strength	200% of working voltage
Quality Factor (Q)	5000 or greater
Insulation Resistance	10 <sup>16</sup> Megohms
Operating Temperature	-55°C to 150°C
Temperature Coefficient	50 ppm/°C
Tuning Torque	4 inch ounces (max)

### Ordering Instructions

Style	RP-VC	10 - 12 - 25	Lead Option
		Kv (Peak) Test	
		Max. Capacitance rating expressed in picofarads (pF)	

### Design

PTFE anode and mount surfaces are metalized with electro-deposited copper. Polyflon's proprietary plating process eliminates the possibility of air being trapped between the PTFE and copper innerface which could break down under voltage stress.

Part Number	Capacitance Range (pF)	Peak (Kv) Working Volts	Peak (Kv) Test Volts	Max. (RMS) Current (amps)	Dimensions/inch (mm)		Wt./Ounces (Approx)
					L(±.020")	Dia.(±.020")	
RP-VC3-6-*	0.3-3	3	6	0.70	0.800 (20.3)	0.375 (9.5)	0.10
RP-VC5-10-*	0.8-5	5	10	2.40	1.250 (31.8)	0.500 (12.7)	0.25
RP-VC8-6-*	3-8	3	6	1.90	0.870 (22.1)	0.560 (14.2)	0.25
RP-VC10-6-*	0.8-10	3	6	1.70	1.150 (29.2)	0.375 (9.5)	0.20
RP-VC10-12-*	0.8-10	6	12	3.40	1.530 (38.9)	0.625 (15.9)	0.75
RP-VC18-2-*	0.8-18	1	2	1.70	1.150 (29.2)	0.420 (10.7)	0.20
RP-VC25-6-*	5-25	3	6	5.50	1.430 (36.3)	0.875 (22.2)	1.00
RP-VC25-6B-*	5-25	3	6	3.90	1.540 (39.1)	0.625 (15.9)	1.00
RP-VC25-15-*	5-25	10	15	7.20	1.770 (45.0)	1.125 (28.6)	1.75

\*Add code number for leads. See lead code number table below.

### Notes

- Working volts and maximum RMS current must not occur simultaneously.
- Peak test voltage rating may be used for pulsed voltage applications. Peak pulsed current will be limited by the duty cycle that will produce an average current that does not exceed the maximum RMS current.
- Mounting Dimension: 1/4" diameter "D" hole. Hardware: 1/4-32 hex nut and internal tooth lockwasher. Mounting flange is at the bottom of the capacitor.

### Lead Option Table

05	without lead wires
15	3" wire, top only - in line with flat
25	3" wire, top and bottom - in line with flat
35	1-1/2" strap, top only - in line with flat
65	3" wire, top only, opposite flat
75	3" wire, top and bottom - opposite flat
85	1-1/2" strap, top only - opposite flat



The only significant degradation we encountered was in the efficiency with which the decoupler field was coupled to the sample ( $\gamma B_2/2\pi$  was reduced by about 40% for the same output power). This was perhaps not surprising but an adequate effective decoupling field could still be obtained and this phenomenon was not further investigated.

We were thus able to obtain quite satisfactory spectra for other projects, which required this probe, without removing the gradient coils.

Yours sincerely,

*W. A. Bubb*

Dr W.A. Bubb

*W. S. Price*

W.S. Price

*Philip W. Kuchel*

Prof P.W. Kuchel

:AD

---

#### In-vivo NMR Spectroscopy

The Department of Radiology of the University of Iowa invites applications for a position in NMR spectroscopy. The University Hospitals is obtaining a 1.5T whole body MR system with spectroscopic capabilities and will be initiating research aimed towards eventual clinical application of in-vivo MR spectroscopy. MR imaging is currently performed on a 0.5T system. The successful candidate will develop an active research program and collaborate with other investigators. A Ph.D. in Chemistry, Biochemistry or related field is required. Experience with in-vivo NMR is preferred.

Contact: E.A. Franken, Jr., M.D.,  
Chairman, Department of Radiology, University of Iowa,  
Iowa City, Iowa 52242. The University of Iowa is an  
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Institut für Molekularbiologie und Biophysik

Prof. Dr. K. Wüthrich

HPM-Gebäude

Durchwahl-Nr.: 01 / 377 24 73

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Postadresse:

Institut für Molekularbiologie  
und Biophysik  
ETH-Hönggerberg  
CH-8093 Zürich

Prof. Bernard Shapiro  
Dept. of Chemistry  
Texas A & M University

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College Station, TX 778

USA

Zurich, July 14, 1987/hu  
(Received 22 July 1987)

Title: SPHINX and LINSHA for the Simulation of 2D NMR spectra

Dear Barry,

Recently we wrote the program SPHINX (Simulation of Pulse sequences in High resolution Nmr experiments) to compute 2D NMR experiments in which the correlation peaks manifest weak or strong homonuclear or heteronuclear scalar coupling [1]. To enable a quantitative comparison with the experiments the line widths, acquisition times  $t_{1,max}$  and  $t_{2,max}$ , filter functions, and the digital resolution are introduced in a second program LINSHA (LINE SHApe simulation program) [1], which can be used to represent the spectra, e.g., as contour plots. Using these programs we computed an "atlas" of cross peak fine structures for spin systems in 2D  $^1H$  NMR spectra of polypeptides and polydeoxynucleotides [2].

Here we demonstrate the use of the programs SPHINX and LINSHA to represent a threonyl spin system in COSY, 2QF-COSY, and RELAYED-COSY spectra (Fig.1). Note the weak, virtual peaks between  $\gamma CH_3$  and  $C^\alpha H$  in COSY and 2QF-COSY, which are due to strong coupling between  $C^\alpha H$  and  $C^\beta H$ . The programs are available upon request (free for University laboratories, at a modest price for profit-oriented organisations; in all cases send a tape with your request).

Best regards,

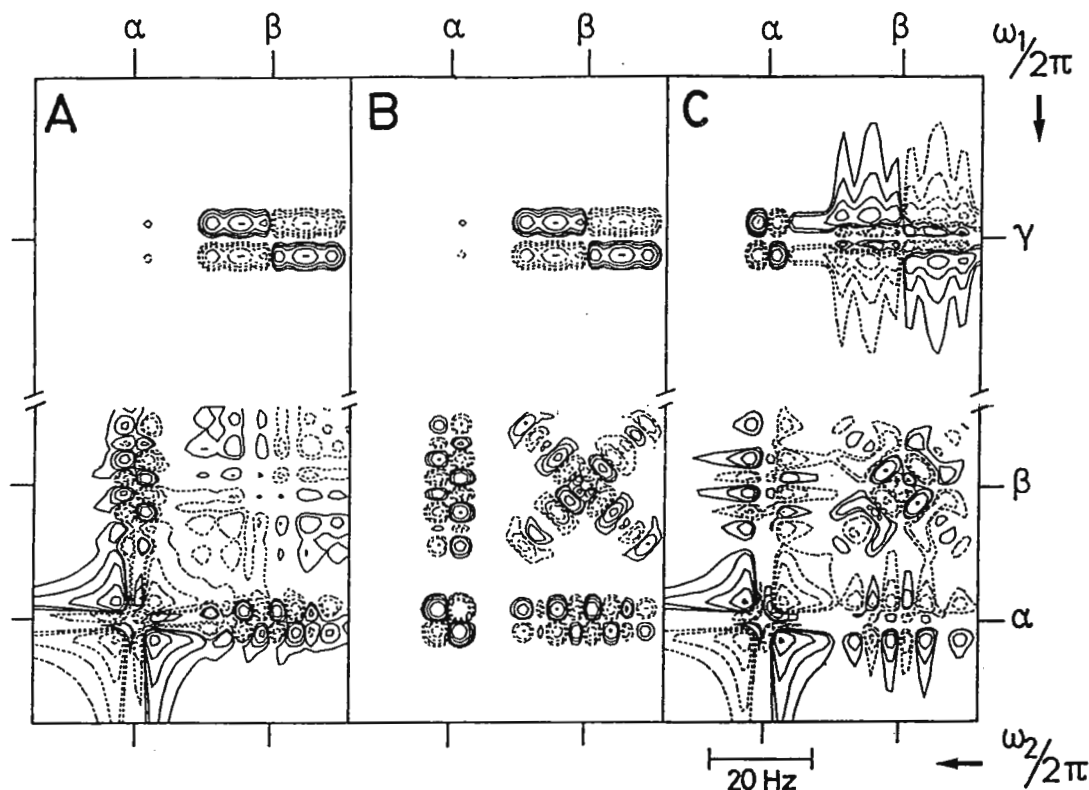
Yours sincerely,

*Hans Widmer*

H. Widmer

*Kurt Wüthrich*

K. Wüthrich



**Fig. 1** Simulations of COSY (A), 2QF-COSY (B), and RELAYED-COSY (total mixing time 50 ms) (C) spectra of Thr with the following parameters:  $J_{\alpha\beta} = 4.0$  Hz,  $J_{\beta\gamma} = 6.3$  Hz,  $\nu_{\alpha} = 0$  Hz,  $\nu_{\beta} = -25$  Hz,  $\nu_{\gamma} = -1000$  Hz, line width = 2.5 Hz,  $t_{1,\max} = t_{2,\max} = 0.381$  s; in both dimensions a sine bell shifted by  $\pi/6$  was used and the digital resolution is 1.0 Hz/point. The frequency scale is the same for  $\omega_1$  and  $\omega_2$ , and  $\alpha$ ,  $\beta$ , and  $\gamma$  identify the chemical shifts of the corresponding protons. The contours are plotted at exponentially increasing positive (solid lines) and negative (broken lines) levels.

#### REFERENCES

- [1] Widmer, H. and Wüthrich, K. (1986) *J. Magn. Reson.* **70**, 270-279.
- [2] Widmer, H. and Wüthrich, K. (1987) *J. Magn. Reson.*, in press.



**SOPHISTICATED INSTRUMENTS FACILITY**  
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**INDIAN INSTITUTE OF SCIENCE**  
 BANGALORE-560 012 INDIA  
 Professor C.L. Khetrpal



Ref. :

Professor Bernard L. Shapiro  
 Texas A&M University  
 College Station  
 TEXAS 77843-3255

Setting the Magic Angle  
Using NMR Spectra of  
Oriented Molecules

Date : June 29, 1987  
 (Received 27 July 1987)

Dear Professor Shapiro,

It may be of interest to report in this letter, a novel and convenient method for setting the Magic Angle using NMR spectra of oriented molecules.

The Use of the  $^{13}\text{C}$  NMR spectrum of chloroform (with natural abundance of  $^{13}\text{C}$  oriented in the nematic phase of a solvent such as ZLI-1167 may be made for such a purpose). Typical spectra at various angles are shown in Fig. 1. The spectra show doublets with separations equal to  $|J(^{13}\text{CH}) + 2D(^{13}\text{CH})|$  where  $J(^{13}\text{CH})$  and  $D(^{13}\text{CH})$  are the indirect and the direct  $^{13}\text{C}$ -H couplings, respectively. The bottom-most trace (trace A in Fig. 1) is the usual decoupled spectrum providing a singlet at the centre of the doublet. The figure also shows that the doublet separation changes with the angle  $\Theta$  which the spinning axis makes with the magnetic field (traces B to F). Such a variation of the doublet separation can be interpreted in terms of the dynamics of the nematic director when the sample is spun around an axis making an angle with the magnetic field. For spinning speeds above a critical value, the director aligns parallel or perpendicular to the spinning axis depending upon the sign of the diamagnetic susceptibility anisotropy of the liquid crystal and the angle  $\Theta$ , all the anisotropic interactions being scaled by a factor  $\Delta = 1/2(3 \cos^2 \Theta - 1)$  or  $-1/2 \Delta$ , respectively. The technique is quite different from the fast magic-angle spinning normally used in high-resolution NMR in solids since in this case the spinning is solely for the purpose of reorienting the director. This can be achieved at much lower spinning speeds than those required in solids. At the exact magic angle,  $D(^{13}\text{CH})$  vanishes and hence the doublet separation corresponds to  $J(^{13}\text{CH})$  (210 Hz in this case). In this case,  $J(^{13}\text{CH})$  and  $D(^{13}\text{CH})$  have opposite signs. The experiment, therefore, involves the determination of the doublet separation as a function of the angle  $\Theta$ . The separation equal to  $J(^{13}\text{CH})$  (210 Hz in this case) corresponds either to the exact magic angle (trace C in the figure) or to the angle which corresponds to  $D(^{13}\text{CH}) = -J(^{13}\text{CH})$  (since the sign of the splitting is not known). The two possibilities can be conveniently distinguished since a slight increase or decrease in the angle decreases the splitting if the angle corresponds to the magic angle where as the splitting increases in one direction and decreases in the other for the situation  $D(^{13}\text{CH}) = -J(^{13}\text{CH})$ .

Yours sincerely,

*C.L. Khetrpal*



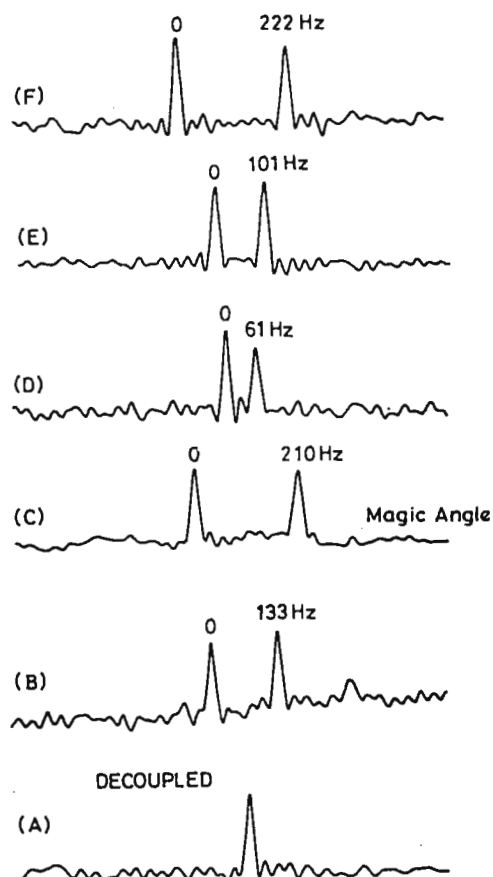


FIG. 1.  $^{13}\text{C}$  NMR spectra of chloroform oriented in the nematic phase of ZLI-1167 recorded on a Bruker MSL-300 spectrometer, as a function of the angle  $\theta$  which the spinning axis makes with the magnetic field. Solute concentration, 10 wt%; temperature,  $18^\circ\text{C}$ ; spinning rate, 1.2 kHz. The spectra were recorded at 75.47 MHz using a double-bearing MASS probe. The angle increases by  $2^\circ$  between the consecutive traces in going from (B) to (F).

#### Position Available

NMR Instrumentation Scientist/Engineer. Doty Scientific, Inc. has an opening for a highly qualified person to fill a position involving interaction with scientific clients and the design and development, from concept to finished product, of state-of-the-art instruments. The successful applicant will have completed studies in E&M, electronics, mechanics, thermodynamics, chemistry, quantum mechanics, material science, scientific instrumentation and NMR. In addition, he or she will have demonstrated a strong interest in hands-on design and development of interdisciplinary electronic instrumentation, and will be familiar with a wide range of manufacturing technologies. Starting salary range: 30-45K, full benefit package. Please send resume, in confidence, to Dr. F. David Doty, Doty Scientific, Inc., 600 Clemson Road, Columbia, SC 29223.

THE STATE UNIVERSITY OF NEW JERSEY  
**RUTGERS**

Department of Chemistry • Wright and Rieman Laboratories  
 New Brunswick • 201/932-2618 • Postal Address: P.O. Box 939 • Piscataway • New Jersey 08855-0939

July 20, 1987

(Received 29 July 1987)

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

RE: Transfer of Data from Varian Spectrometers  
 to VAX Computers

Dear Barry:

The Chemistry Department at Rutgers currently has three high field spectrometers consisting of a Varian XL-400, a VXR-200, and are awaiting installation of a VXR-500. We were not initially satisfied with the flexibility of Varian's 2D NMR processing software on the XL-400 and so we set up Dennis Hare's FTNMR program on our VAX computers. The first requirement for off-line data processing is an efficient method for transferring data from the spectrometer to other computers. We initially used a RS-232 linkage with Varian's serial communication software to transfer data. This procedure was excruciatingly slow, taking 15 hours to transfer a 1K by 1K data set. For the past year we have used Varian's Ethernet hardware and software to transfer data from the XL-400 to a micro VAX II computer. Varian's Ethernet package is very efficient with a 2K x 1K data set requiring only 8 minutes to transfer.

The next step in processing the Varian data on the VAX is to convert it to FTNMR format. We have a program, VARCON, written by Dennis Hare that converts Varian data to FTNMR format. (This program is part of the FTNMR package supplied by Dennis Hare through M & R Resources, P.O. Box 642, Ashburnham, MA 01430 or can be obtained by writing directly to me.) For this program to function properly the following procedure must be used.

A) Data must be acquired with DP=Y. This creates a 32 bit word instead of a 16 bit word and makes it straightforward to convert it to VAX format. We always acquire data with DP = Y since we have a 15 bit digitizer on the spectrometer, and a 16 bit word is obviously not sufficient to handle more than a few scans.

B) The data must be saved with the SVCF command. This command "compresses" the data so parameters are only stored with the first FID in a multi-FID experiment such as a 2D NMR file. The only limitation of this command, compared to the normal SVF command, is that you cannot restart an experiment that has been stored with SVCF.

C) The Varian Ethernet software is then used to transfer the file and creates a VAX file with undefined format that cannot be read with a FORTRAN program. In order to convert it FORTRAN readable form, we run a VMS command file that consists essentially of a single merge command to convert the file to a defined format. A sample VMS command that accomplishes this is:

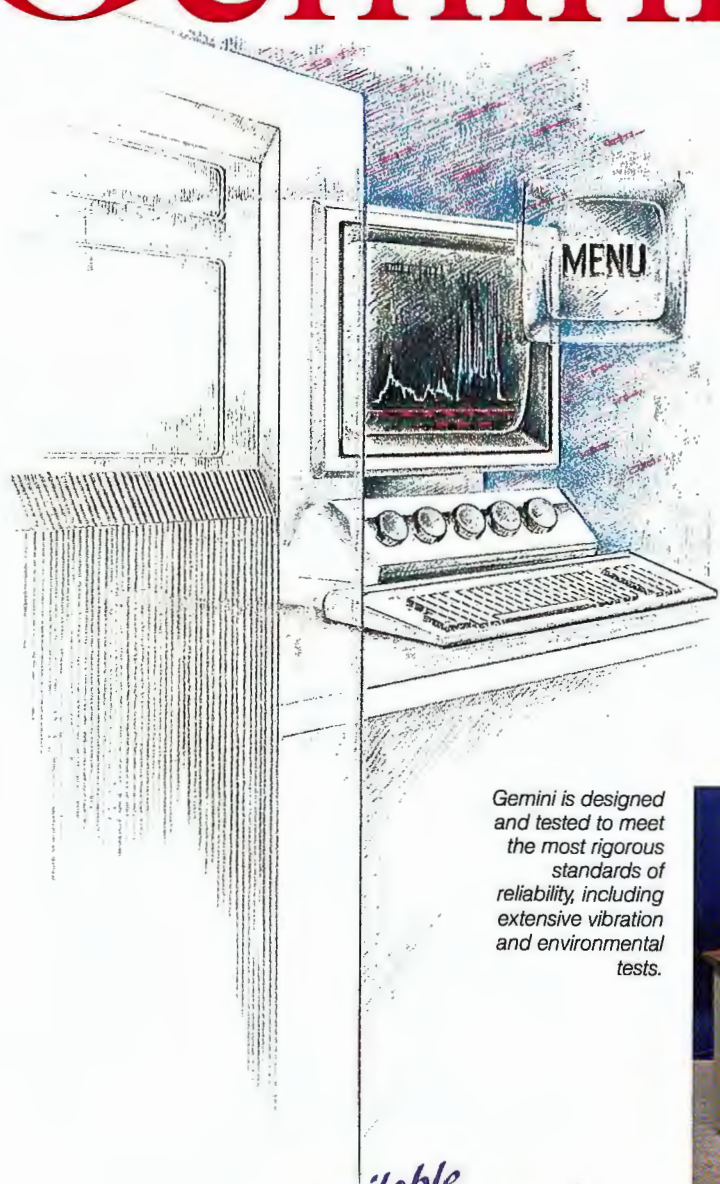
```
$ merge/nocheck filename.dat filename.dat/format = fixed = 512
```

This process is a bit of a nuisance since it doubles the time it takes to convert a file, but without the Varian source code I know of no easier way of creating a FORTRAN readable file.

(continued on page 37)

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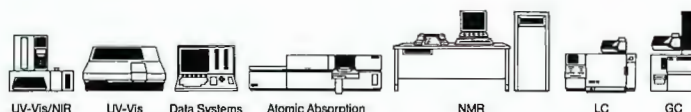
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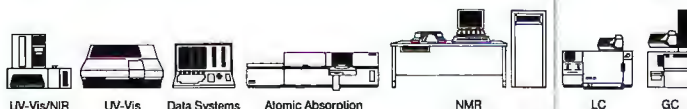
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D) To use the standard VARCON program, you must transfer the whole Varian file, which actually consists of five separate files with the last one being all the FIDs. The VARCON program skips the correct number of blocks so that it starts converting the data at the beginning of the first FID. The present version of VARCON is not able to read the parameters in the Varian file and so the user must supply the correct NP (number of points in Varian nomenclature). This is rather inconvenient and if anyone has a simple FORTRAN routine for reading Varian parameters, I would like to hear about it.

E) The data has now been converted and is ready to be read into D. Hare's wonderfully flexible FTNMR program.

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I hope this will be of some help to anyone trying to process Varian data on an off-line computer.

Sincerely yours,

Arthur Pardi  
Assistant Professor

---

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TJB:RD/TGB12

15th July 1987

(Received 27 July 1987)

Room Temperature  $^{14}\text{N}$  Spectrum of  $\text{NH}_4\text{ClO}_4$ 

Professor Bernard L. Shapiro  
 Texas A & M University  
 Department of Chemistry  
 College Station  
 TEXAS 77843-3255

Dear Professor Shapiro,

In the course of a  $^{35,37}\text{Cl}$  and  $^2\text{H}$  NMR investigation [1] of the legitimacy of a previously described phase transition in  $\text{NH}_4\text{ClO}_4$  [2], we have observed the  $^{14}\text{N}$  spectrum at 296 K for the protonated and deuterated forms. In both cases all the features of an  $I = 1$  spectrum are clearly displayed, which enables both  $e^2qQ/h$  and  $\eta$  to be obtained. We had intended to make  $T_1$  measurements but the time required to obtain sufficient signal to noise prevented this.

In case these results are of interest to your readers we display a representative spectrum below along with a tabulation of the coupling constants and asymmetry parameters.

The spectrometer was a Bruker MSL 400 operating at a frequency, for  $^{14}\text{N}$ , of 28.908 MHz. We used a solid echo pulse sequence with phase alternation. The samples were BDH AR grade.

Yours sincerely,

T.J. Bastow

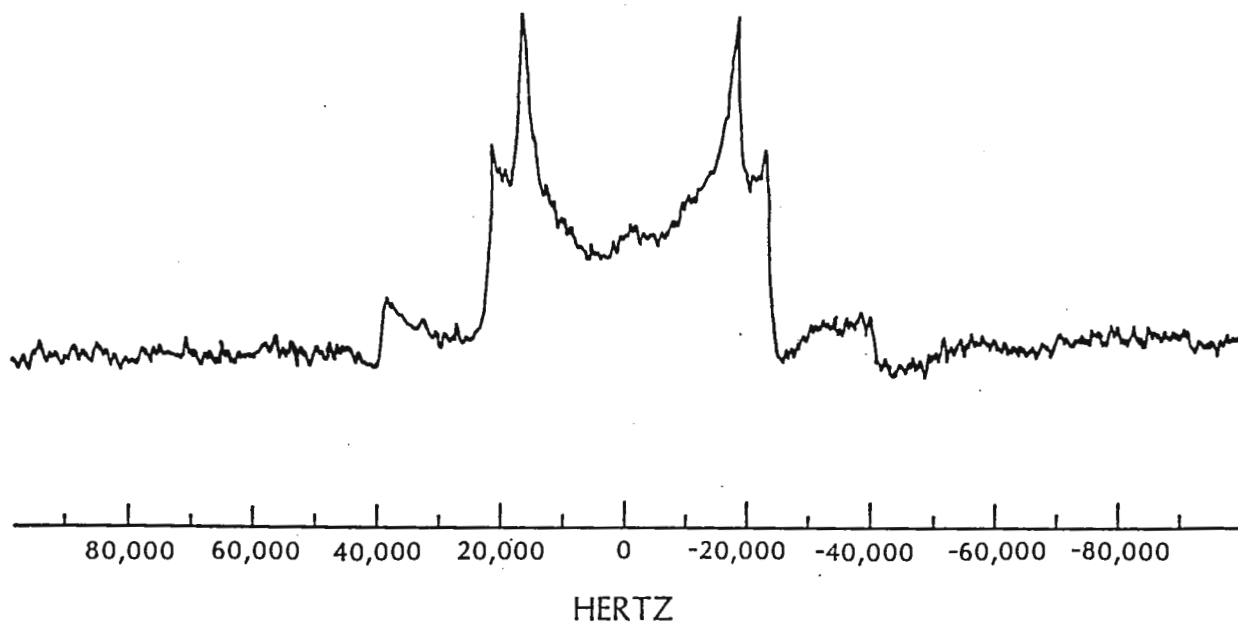
G.W. West

	$e^2qQ/h$ (kHz)	$\eta$
$\text{NH}_4\text{ClO}_4$	53.3	0.13
$\text{ND}_4\text{ClO}_4$	52.2	0.11

## References

- [1] T.J. Bastow, R.J.C. Brown and S.L. Segel, J. Chem. Phys. - to be published  
 [2] T. Chakraborty, S.S. Khatri and A.L. Verma, J. Chem. Phys., 84, 7018 (1986)

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$^{14}\text{N}$  in  $\text{NH}_4\text{ClO}_4$ 

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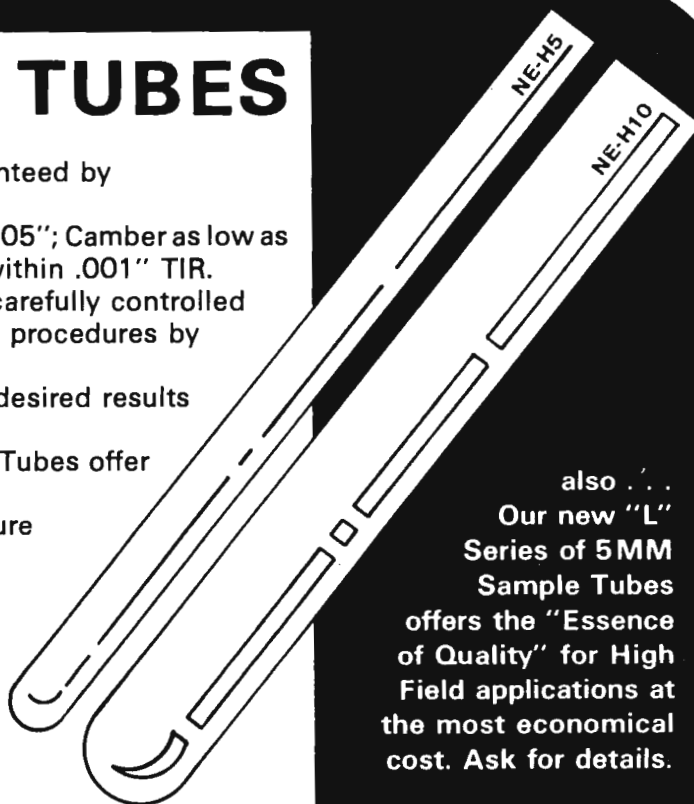
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504/388-3361

July 22, 1987

(Received 27 July 1987)

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

Inequivalent C-<sup>2</sup>H Sites Adjacent  
to Carboxylic Acids

Dear Professor Shapiro:

We are using adiabatic demagnetization in the laboratory frame (ADLF) spectroscopy to obtain high resolution solid-state deuterium spectra of C-<sup>2</sup>H bonds. Based on the work by Hiyama *et al.* (*J. Am. Chem. Soc.*, **1987**, *109*, 2525), we expected to observe inequivalent sites in C<sup>2</sup>H<sub>2</sub> groups adjacent to carboxylic acid groups.

Substituted acetic acids crystallize about a center of symmetry. With substituents such as (4-chlorophenyl)-, the two C-<sup>2</sup>H bonds on the carbon adjacent to the acid group are held at a known orientation; the essential results of a single crystal X-ray diffraction experiment are shown in Fig 1.

Fig 2 shows the ADLF spectra taken at 77 K; there are two distinct C-<sup>2</sup>H sites. Based upon *ab initio* molecular orbital calculations of acetic acid and phenylacetic acid dimers, we assign the sites as: H1(C2),  $e^2qQ/h = 174.0(9)$  kHz,  $\eta = 0.034(16)$ ; H2(C2),  $e^2qQ/h = 168.0(9)$  kHz,  $\eta = 0.024(17)$ . Succinic acid also showed inequivalent C-<sup>2</sup>H sites in a single crystal study done using distant ENDOR spectroscopy (Boroske, *et al.* *J. Magn. Reson.* **1979**, *35*, 231). We are now exploring the generality of this phenomenon and are attempting to develop a Karplus-type relationship for the measurement of <sup>2</sup>H-C-C-X torsion angles from solid-state deuterium NMR spectroscopy.

Sincerely,



Les Butler  
Assistant Professor of Inorganic Chemistry

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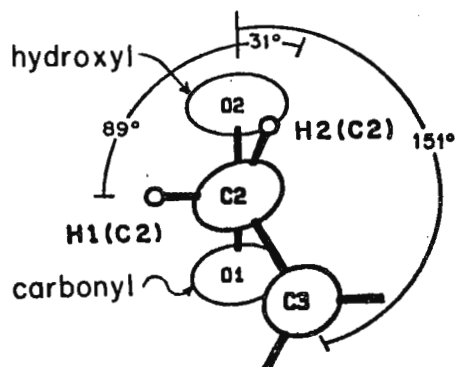


Fig 1. Relative orientation of the carboxyl acid group and the  $\text{CD}_2$  unit. Viewed along the  $\text{CD}_2(\text{C}_6\text{H}_5)\text{-CO}_2\text{H}$  bond.

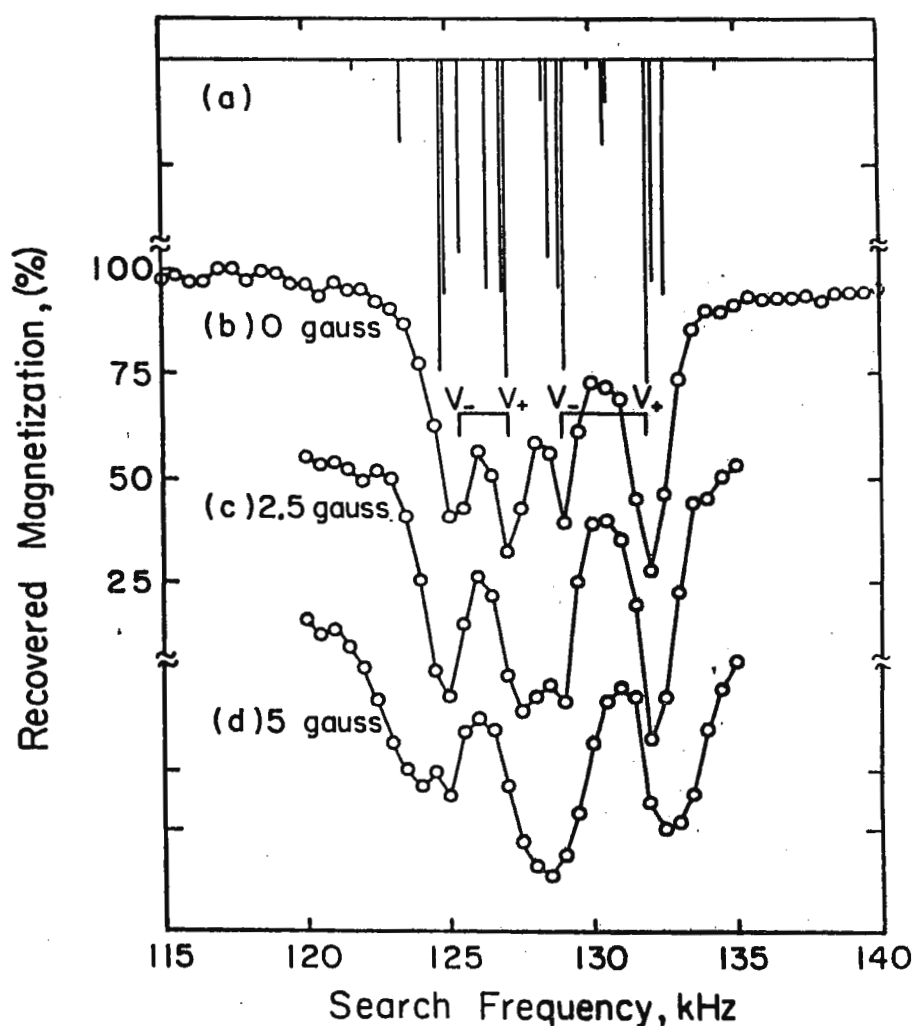


Fig 2. Deuterium ADLF spectra of (4-chlorophenyl)(2,2- $^2\text{H}_2$ )acetic acid taken at 77 K with 0.5 kHz search frequency increments. (a) The calculated fine structure for a  $\text{CD}_2$  unit. Assignment of transitions based upon frequency shifts caused by a small applied magnetic field: (b) 0 gauss, (c) 2.5 gauss, and (d) 5 gauss.



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(Received 3 August 1987)

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

<sup>13</sup>C NMR Study  
"Glucose Metabolism of Oxygenated Human Red Blood Cells"

Dear Professor Shapiro:

Glucose metabolism of human red blood cells was investigated using carbon-13 nuclear magnetic resonance spectroscopy. Oxygenation of RBC with <sup>13</sup>C1 glucose as substrate, produced NMR resonances assigned to <sup>13</sup>C6 glucose, <sup>13</sup>C4 glucose, <sup>13</sup>C3 glucose/ <sup>13</sup>C3 glucose-6-phosphate, <sup>13</sup>C3 lactate and <sup>13</sup>C3 3-phosphoglycerate/2,3-bisphosphoglycerate (Figure 1). These assignments were made on the basis of previously reported chemical shifts.<sup>1</sup> The data suggests that the reversal of glycolysis takes place in oxygenated blood. This is evident from the formation of <sup>13</sup>C labeled C4/C6 glucose and C3 glucose/C3 glucose-6-phosphate. For this scrambling to occur the <sup>13</sup>C-1 glucose had to be metabolized to triosphosphates followed by a reversal through aldolase. The scrambling of the <sup>13</sup>C label in glucose can occur since the existence of nonspecific phosphatases in RBC is known,<sup>2</sup> making the hydrolysis of hexose phosphates to hexose possible.

Presently, the <sup>13</sup>C4 and <sup>13</sup>C3 glucose assignments are tentative since there is no known biochemical pathway by which <sup>13</sup>C1 label can scramble to the C3 or C4 position. But the fact remains that chemical shifts at 70.4 and 76 ppm appear, suggesting the presence of <sup>13</sup>C4 and <sup>13</sup>C3 glucose. None of the other three carbon metabolites in the glycolytic pathway were found to resonate at 70.4 or 76 ppm. Further investigations are underway to unequivocally establish the identity of these resonances.

These results show that the reversal of 3-phosphoglyceraldehyde to glucose is in competition with its catabolism to lactate.

(continued on page 45)

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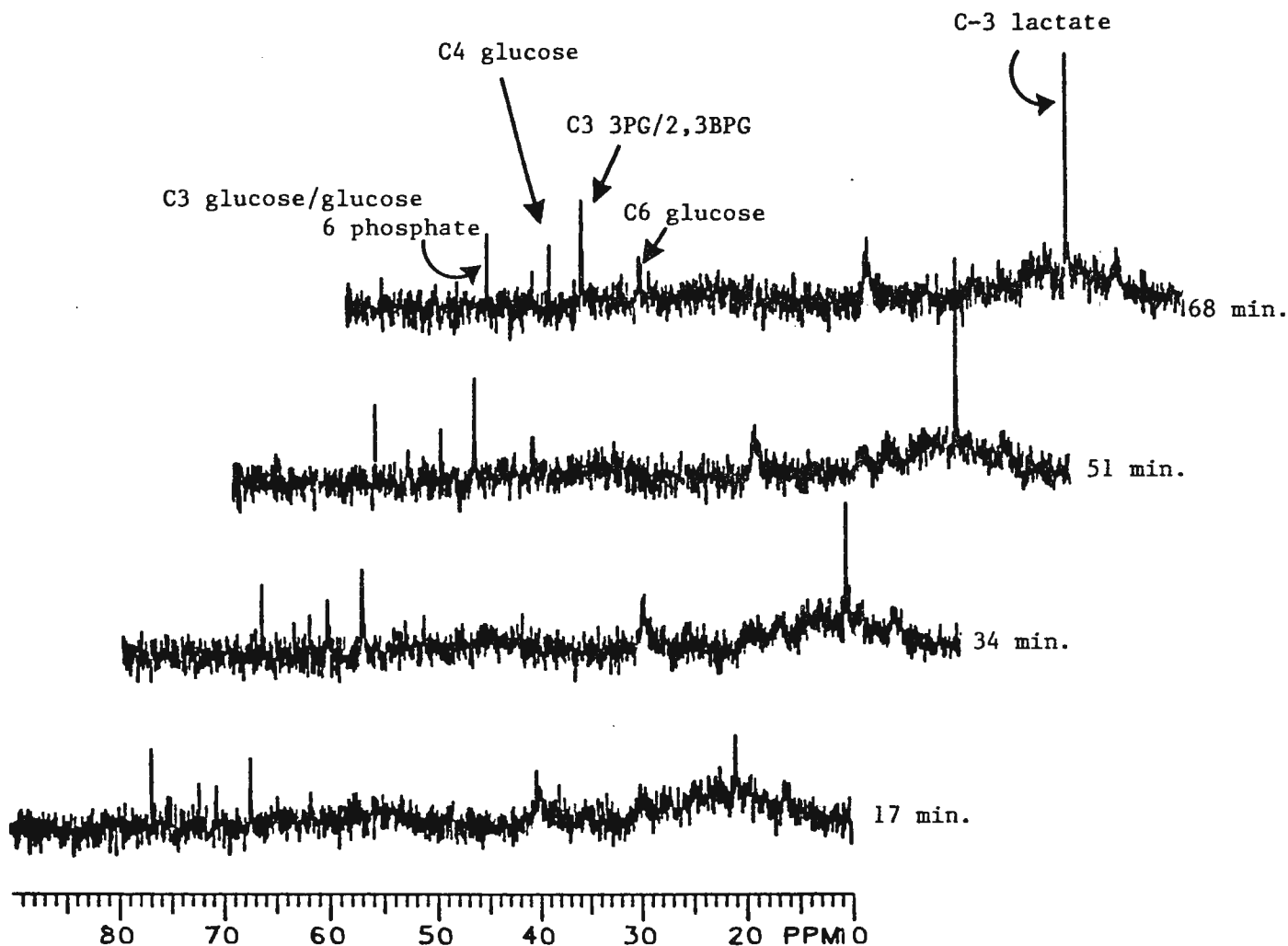


Figure 1. A  $^{13}\text{C}$  NMR time course from oxygenated human RBC metabolizing  $^{13}\text{C}$ -1 glucose. Four spectra were accumulated each consisting of 1024 scans. The total acquisition time was 68 minutes.

Sincerely,

*Nina C. Gonnella*

Nina C. Gonnella, Ph.D.

*Geetha Ghai*

Geetha Ghai, Ph.D.

1. Canioni, P., Alger, J.R. and Shulman, R.G., *Biochem.* **22**, 4974 (1983).
2. Komoda, T., Koyama, I., Hasegawa, M. and Sakagishi, Y., *Rinsho Byori.* **31**, 682 (1983).



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## DEPARTMENT OF CHEMISTRY

CHEMISTRY BUILDING

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

July 20, 1987  
(Received 29 July 1987)

"Total Assignment of Carbon-13 NMR Spectrum of 10-Oxo-14  
iodohecateryclo [6.6.0.<sup>2,6</sup>.0<sup>3,13</sup>.0<sup>4,11</sup>.0<sup>5,9</sup>] tetradecane (1)"

Dear Professor Shapiro:

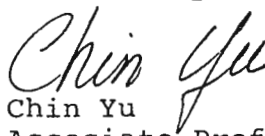
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TAMUNMR newsletter.

The ketoidide (1) have attracted many organic and theoretical chemists' interest for its cage geometry. Moreover, it might be used for a more efficient synthesis of dodecanhedrane.

To complete analysis the <sup>13</sup>C spectrum of 1, the double quantum NMR proved to be the best method as showed in the Figure 1.

The double quantum NMR experiment was carried out in MSL-200 instrument with 5 mm dual probe by the pulse sequence: 90°-τ-180°-τ-90°-ACQ, as proposed by Turner. τ was set for 7 ms and 64 FIDs were generated. A 90° shifted sine-bell window function was applied on both dimensions before Fourier transformation. A total of 16 <sup>13</sup>C-<sup>13</sup>C connectivities were observed (the carbonyl group was not included), allowing complete assignment of C-13 spectrum from this experiment along.

Yours truly,



Chin Yu  
Associate Professor of Chemistry

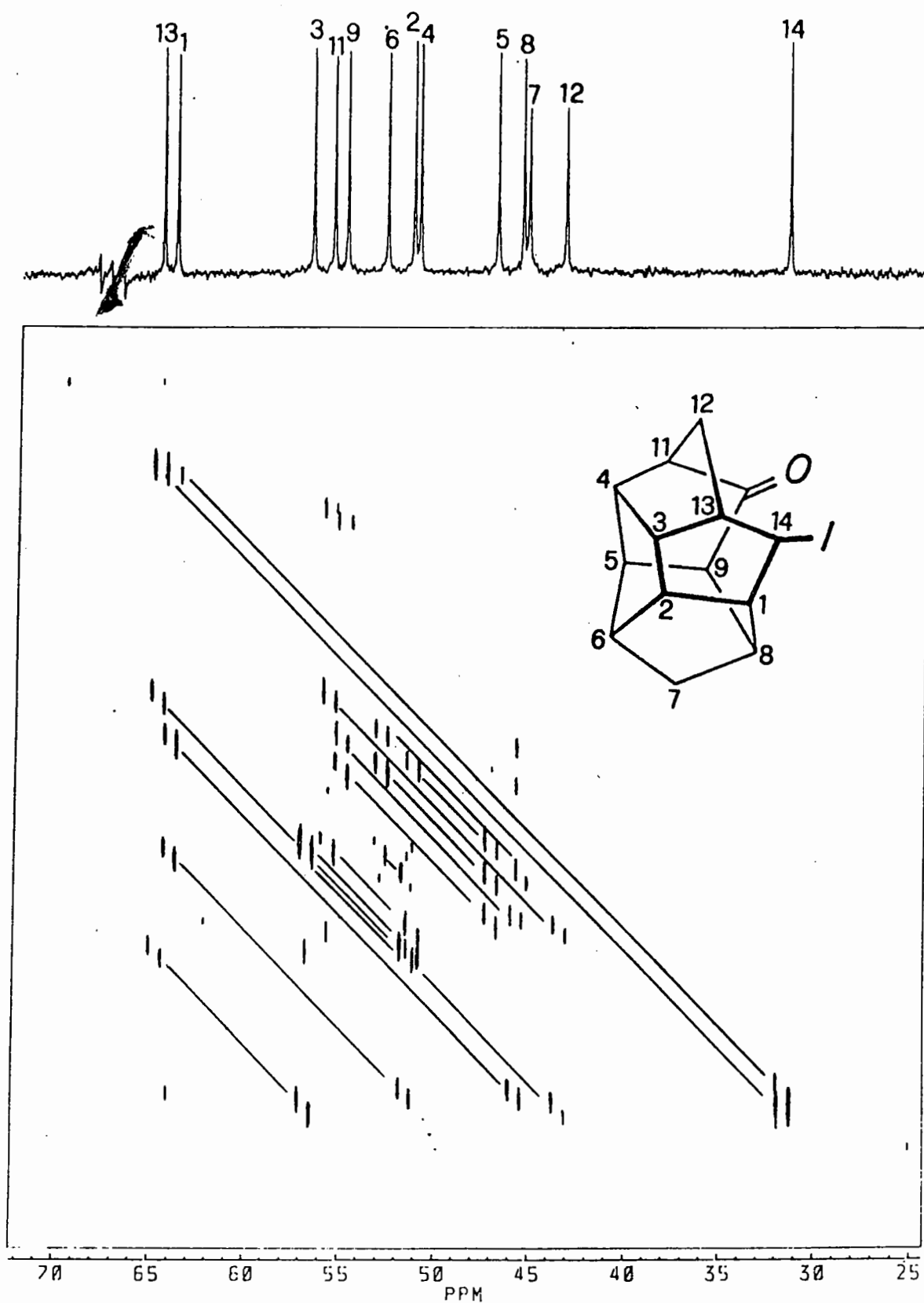


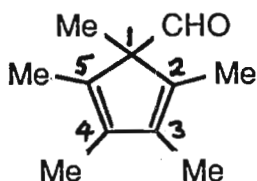
Figure 1. Double quantum  $^{13}\text{C}$  NMR spectrum of 10-Oxo-14-iodohecatetradecano [6.6.0.2,6.0<sup>3,13</sup>.0<sup>4,11</sup>.0<sup>5,9</sup>] tetracycane

University of Leeds  
 Department of Organic Chemistry  
 Woodhouse Lane  
 Leeds LS2 9JT  
 U.K.  
 22/07/87 (Received 29 July 1987)

'Resonance Assignments for a Fluxional Cyclopentadiene Derivative'

Dear Professor Shapiro,

A number of years ago, two of my colleagues at Leeds reported the temperature dependence of the  $^1\text{H}$  NMR spectrum of 1-formyl-1,2,3,4,5-pentamethylcyclopenta-1,3-diene, **1**, in which the formyl group undergoes a rapid ( $k \sim 90\text{s}^{-1}$  at 298K), degenerate sigmatropic migration around the ring [1]. As was suggested in the original paper, and was pointed out by Sandström in his book on dynamic NMR [2], the details of the mechanism of this process depend crucially on the assignments of the resonances in the original spectrum. These were initially arrived at by comparison with other pentamethylcyclopentadiene derivatives. This note describes the unambiguous assignment of the  $^1\text{H}$  and  $^{13}\text{C}$  spectra of **1** at low temperature, and hence confirms the mechanistic pathway.



**1**

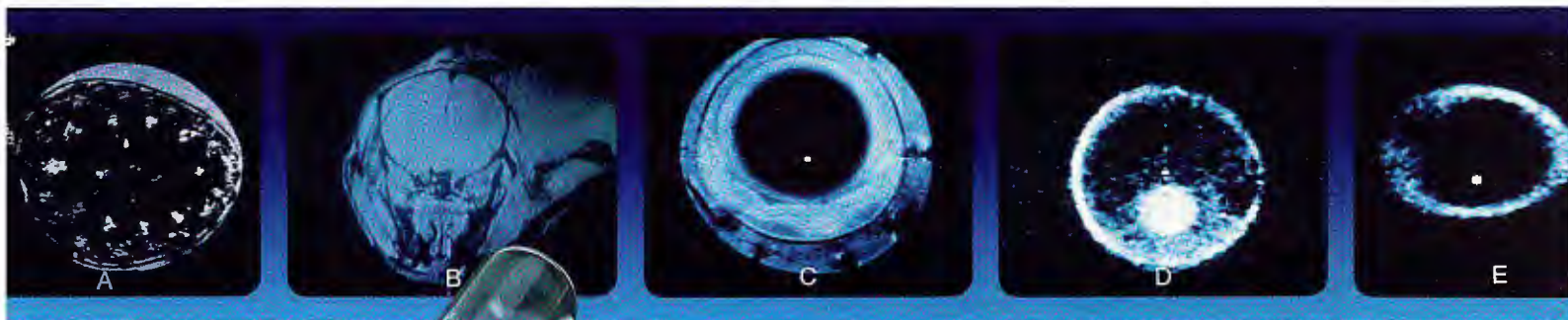
The  $^1\text{H}$  and  $^{13}\text{C}$  spectra of **1** in  $\text{CD}_2\text{Cl}_2$  are essentially temperature independent below 243K. Figure B shows part of a 'long-range' CH COSY experiment at 230K (optimised for  $J_{\text{CH}} = 6\text{Hz}$ , a compromise value to show correlations for  $^2J_{\text{CH}}$  and  $^3J_{\text{CH}}$  but not for longer range couplings) which clearly shows two of the ring carbons correlating with two methyls each and the third (at 132.1ppm) correlating with all three. This, together with the straightforward assignment of the resonance of C1 at 70.1ppm and a CH COSY spectrum optimised for one bond couplings, allowed all of the resonances of **1** to be assigned (see Table).

Table of chemical shifts for **1**.

	CHO	C1	C2,C5	C3,C4	1-Me	2,5-Me	3,4-Me
$\partial_{\text{C}}$	196.2	70.1	132.1	141.9	9.7	10.0	11.3
$\partial_{\text{H}}$	7.60	--	--	--	1.17	1.73	1.89

(continued on page 51)

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*Fig. C: A cross sectional image of a mouse eye, 3 mm in diameter. Resolution  $20\mu \times 20\mu \times 250\mu$ .*

*Fig. D: Image of an ovum from laevis (frog egg). Resolution  $10\mu \times 10\mu \times 250\mu$ .*

*Fig. E: Diffusion of water through a piece of nylon. Resolution  $50\mu \times 50\mu \times 1000\mu$ .*

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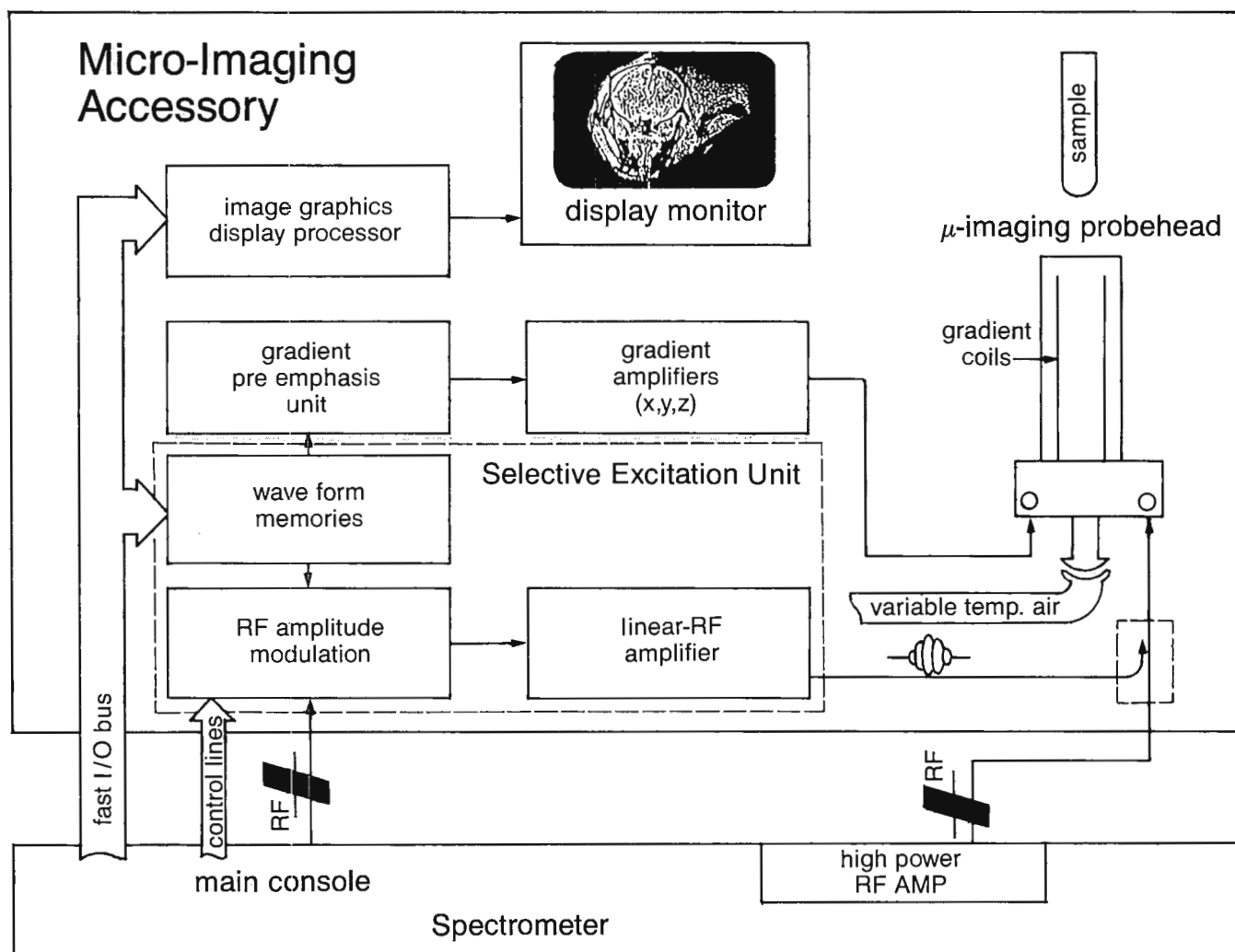
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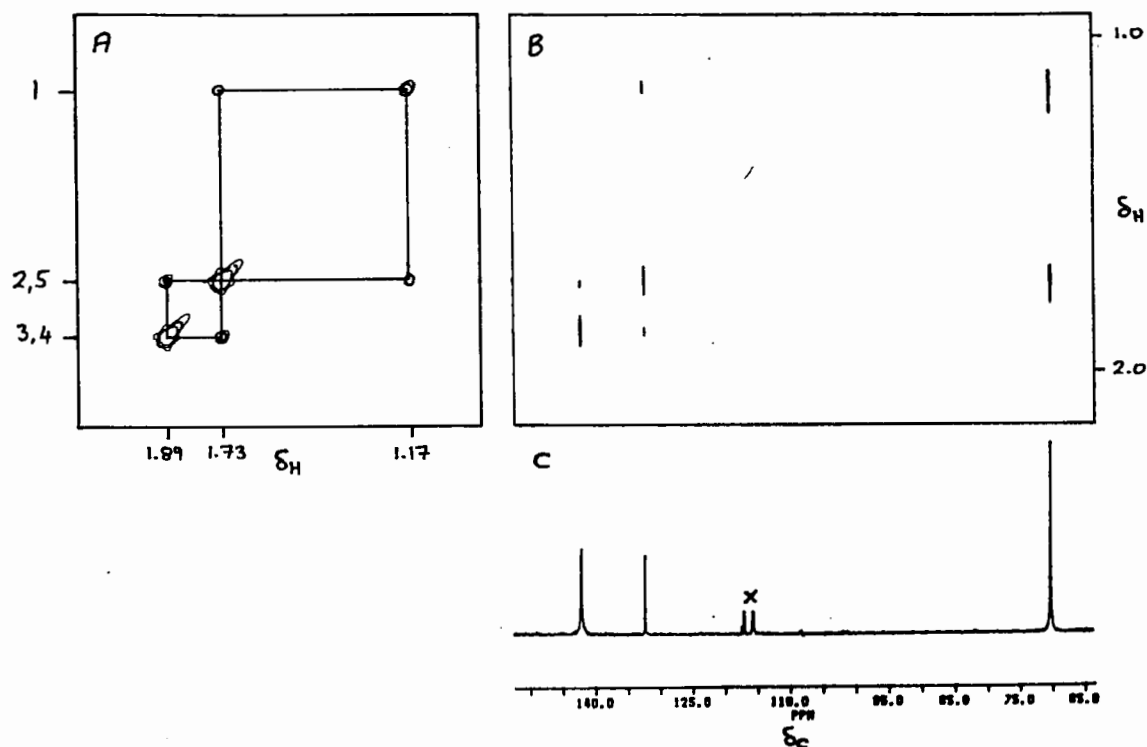
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Sågvägen 12, S-18400 Åkersberga, Sweden  
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The  $^1\text{H}$  assignments were confirmed by recording the NOESY spectrum of **1** at 203K (Fig. A), at which temperature the exchange process is extremely slow ( $k < 0.003\text{s}^{-1}$ ). These assignments are in agreement with those in Bushby and Jones's original paper and confirm that the formyl sigmatropic shift is 1,5 and not 1,3.

A  $^{13}\text{C}$  study of the dynamic behaviour of **1** and related compounds will be reported elsewhere.



**Figures.** Spectra of **1** in  $\text{CD}_2\text{Cl}_2$  recorded on a Brüker AM400.

A)  $^1\text{H}$  NOESY spectrum ( $t_m$  0.7s) at 203K.

B) 'Long-range' CH COSY spectrum at 230K.

C) Part of  $^{13}\text{C}\{-^1\text{H}\}$  spectrum at 230K (peaks marked X are due to impurities).

[1] R.J.Bushby and D.W.Jones, J.C.S.Chem.Comm., 1979, 688.

[2] J.Sandström, 'Dynamic NMR Spectroscopy', Academic Press (London), 1982, 169-171.

Yours sincerely,

*Alistair G. Swanson*

Alistair G. Swanson.

**UNIVERSITÉ CLAUDE BERNARD LYON I**  
**LABORATOIRE DE RESONANCE MAGNETIQUE NUCLEAIRE**

Bâtiment 721  
43, boulevard du 11 Novembre 1918  
69622 VILLEURBANNE Cedex  
Tél. 78 89 81 24 (secrétariat poste 33.70 ou 32.10)

Villeurbanne, July 17, 1987  
(Received 27 July 1987)

Professor B.L. SHAPIRO  
Texas A & M University  
College Station TX 77843 (USA)

**Title : Linear Power Amplifier Setting up on the CXP**

Dear Professor Shapiro,

Presently our NMR biomedical research system consists in a Bruker CXP spectrometer associated with an air core Oxford resistive magnet operating at .15 T. Since we are interested by imaging and any localized observation on medium scale samples (rats, rabbits, ...), we built a 25 cm diameter gradient housing. The gradients coils are monitored by the preamplifier unit through three Crown M-600 power supplies.

Very recently, we had the opportunity to get a LPI-10 linear power amplifier from ENI. Then people in our group are looking for the design of sophisticated r.f. pulses, such as sinc modulated pulses, in spite of the low versatility of the Bruker system. First at all it was necessary to install the LPI-10 and we report here the first setting up we did for multipurpose use. Figure 1. This modification of our machine is too recent to have a good experience of the system ; however we did not notice any trouble yet.

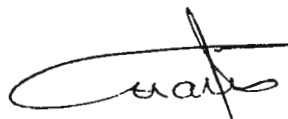
Please, credit his letter to Professor Delmau as a renewal contribution.

Yours truly

A. BRIGUET

H. LAHRECH

P. PIMMEL



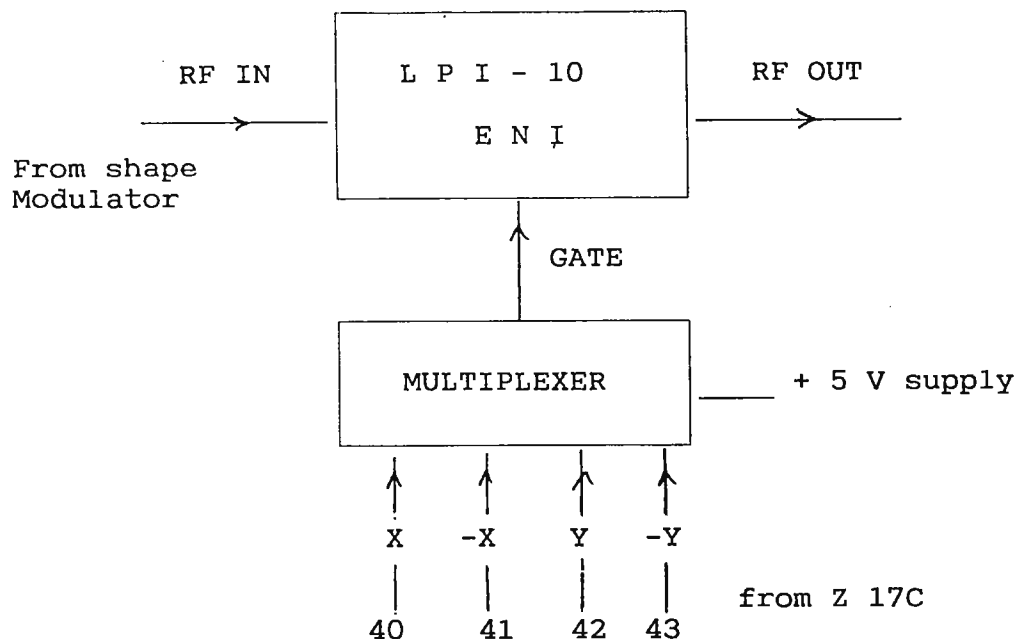


Figure 1 : Schematic for the LPI-10 installation.  
 The multiplexer is made from a 4002 Circuit (two NOR gates, four inputs each)

---

NOTICE: Our XL-100(15) has passed on but we have accessories for sale which are in excellent working condition. They are: Probes-V-4415 w/preamps, spinner, match boxes and inserts; V-4415 w/preamps; V-4412 w/preamps, spinners, match boxes, and extra inserts; V-4418 <sup>13</sup>C (18 mm) complete. We also have an extra set of inserts for any V-4415 probe. A micro probe kit (1.7 mm) is also available. Prices are negotiable. Write: K. D. Berlin, Department of Chemistry, Oklahoma State University, Stillwater, OKLAHOMA 74078 [(405) 624-5950].





July 7, 1987

(Received 13 July 1987)

Observation of Homogeneous Broadening in the  
Presence of Inhomogeneous Broadening

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

Dear Barry:

Local motion can broaden the  $^{13}\text{C}$  MASS signals of solid polymers when it occurs at a rate comparable to the strength of the decoupling irradiation, expressed in frequency units, or the rate of magic-angle spinning. In amorphous materials such as solid polymers, the inhomogeneous broadening resulting from the range of packing environments available to the polymer chain normally obscures any broadening resulting from local motion, however.

Generation of "spike spectra" by Fourier transformation of the entire echo train in a Carr-Purcell experiment (a la Kurt Zilm) provides an easy way to make homogeneous broadening visible in the presence of substantial inhomogeneous broadening. The method works well for non-spinning samples of polymers, in which the inhomogeneous broadening results from the chemical shift anisotropy.\* It is also useful for spinning samples, although the Carr-Purcell train must be synchronized with the spinning. The only other potential problem is that the spikes can be so narrow that the echo train persists for several hundred milliseconds. Some attention to heat buildup during such a long decoupling period is prudent.

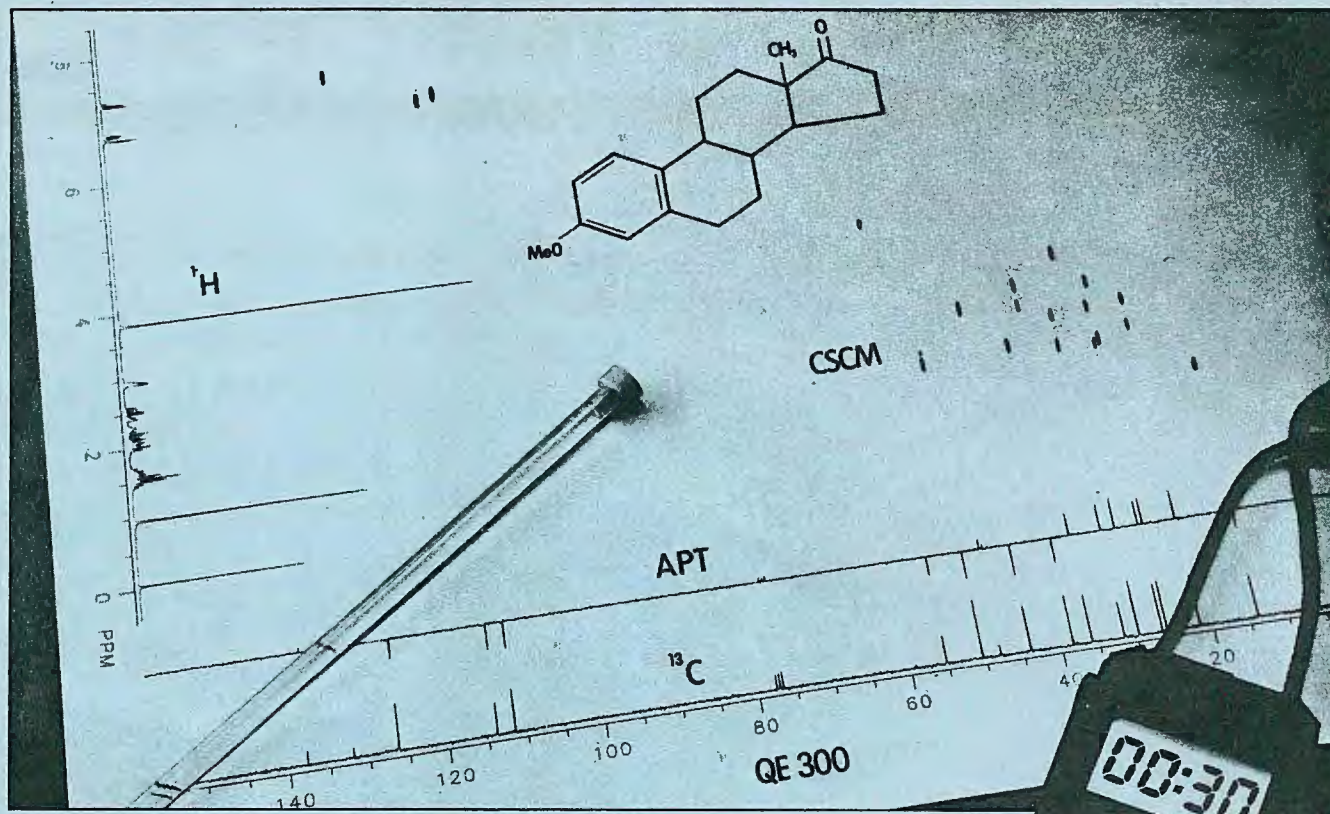
Vince Nicely of the Kodak plant in Tennessee and I have shown that temperature-dependent spike widths can be observed in many polymers whose standard spectra are apparently temperature independent. Examples of the spectra will be included in a manuscript to be submitted soon.

\*S. Swanson, S. Ganapathy, S. Kennedy, P. M. Henrichs, and R. G. Bryant, J. Mag. Reson., 69, 531 (1986).

Very truly yours,

A handwritten signature in cursive script, appearing to read 'Mark', written in dark ink.

P. Mark Henrichs  
Corporate Research Laboratories



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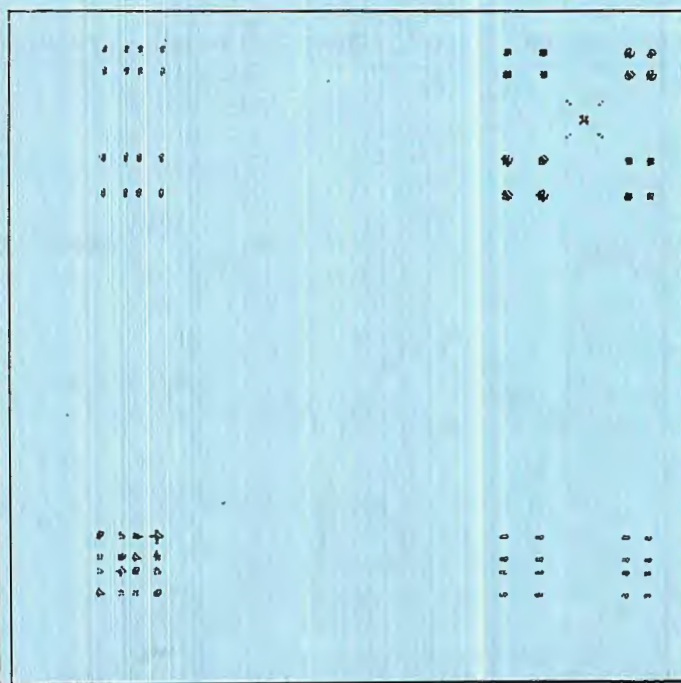
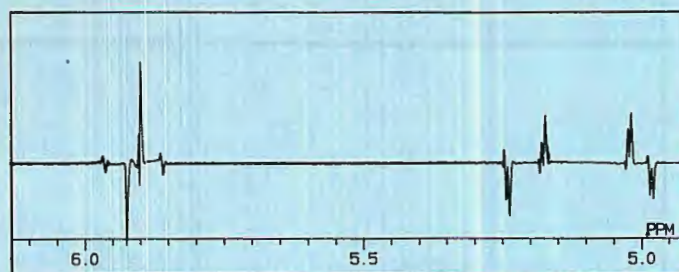
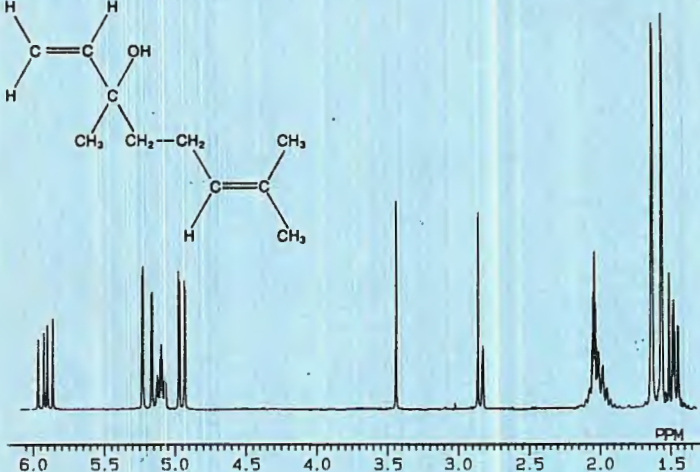
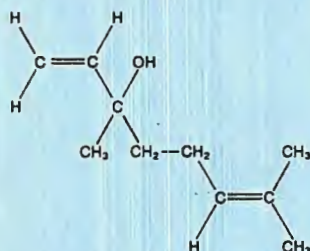
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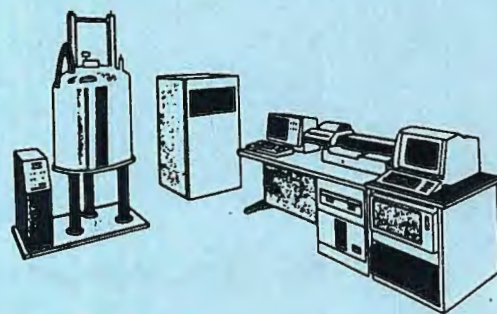
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