

Texas  
A  
M  
&  
University  
N - M - R  
Newsletter

No. 242

November, 1978

K. F. Elgert and R. Kosfeld <sup>13</sup> C NMR Spectroscopy of Poly(vinyl chloride). . . 1	S. L. Patt CRAPS: Homospoil T <sub>1</sub> 's Without the Homospoil. . .26
R. E. Santini, G. W. Kramer and D. C. McCain Diffusion of Ambient Helium into NMR Probe Dewars. . . . . 3	R. K. Harris and A. A. M. Ali Tetraalkyldiphosphines: A Spectroscopic Puzzle Solved . . . . .28
L. Crooks Positions Available . . . . . 5	J. W. Cooper Conversational LAOCN3 . . . . .31
W. B. Moniz, A. N. Garroway, C. F. Poranski and H. A. Resing Postdoctoral Fellowships Available. . . . . 6	R. E. Santini The Purdue Biological NMR Laboratory is Now Open for Business . . . . .33
V. Formacek and K. H. Kubeczka Qualitative and Quantitative Analysis of Essential Oils by <sup>13</sup> C . . . . . 7	
G. C. Levy Postdoctoral Openings In NMR at Florida State University. . . . .11	
C. Lauterbur Postdoctoral Positions Available. . . . .12	
L. Cavalli, G. Cancellieri and L. Lanzini Hydrolysis of Propylene Oxide . . . . .13	
C. H. Robinson and R. J. Highet A Hydrogen Bond Across a 10-Membered Ring . . .16	
P. Laszlo A Grab-Bag of Grabbers. . . . .18	
G. E. Maciel Laboratory Manager Position Available for Regional NMR Center . . . . .20	
K. Roth Selective Measurement of Coupling Constants Between Quaternary Carbons and Phosphorus . . .21	
D. R. Dalton NMR Technician Position Available . . . . .23	

A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.





## WILMAD VIALS AND SEPTUM BOTTLES ADD UTILITY AND ECONOMY TO NMR SAMPLING

Consummate care in the storage and preparation of spectroscopic samples is just as integral a part of good spectroscopic practice as running the investigation or analyzing the spectra. And consummate care, of course, begins with equipment.

Our new, expanded Wilmad line of vials, storage and septum bottles, and a broad variety of stoppers, caps, and septa help materially to simplify the handling, storage, and preparation of samples . . . eliminate expensive sample loss . . . and save unnecessary waste of time and money.

Wilmad vials and bottles are manufactured of top-quality borosilicate glass to prevent any pH modification of the contents. The variety of caps available match any sampling or storage need. Snap caps of polyethylene, open-top types with elastomer septa, aluminum seals with Teflon-faced septa . . . whatever you need we now carry in stock.

Write or call for our new Catalog 781.



### WILMAD GLASS COMPANY, INC.

*World Standard in Ultra Precision Glassware*

Route 40 & Oak Road • Buena, N.J. 08310 U.S.A.

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

TAMU NMR NEWSLETTER - ADVERTISERS

Bruker Instruments, Inc. - see p. 10  
 JEOL Analytical Instruments, Inc. - see p. (i) and outside back cover  
 Nicolet Instrument Corporation - see inside back cover  
 Varian Instrument Division - see p. 24  
 Wilmad Glass Co., Inc. - see inside front cover

TAMU NMR NEWSLETTER - SPONSORS

Abbott Laboratories  
 Bruker Instruments, Inc.  
 Eastman Kodak Company  
 JEOL Analytical Instruments, Inc.  
 Dr. R. Kosfeld, Abt. Kernres., Inst. f. Phys. Chem.,  
 TH Aachen (Germany)  
 The Monsanto Company  
 Nicolet Technology Corp., Palo Alto, CA  
 (formerly Transform Technology, Inc.)  
 Shell Development Company  
 Unilever Research  
 Varian, Analytical Instrument Division

TAMU NMR NEWSLETTER - CONTRIBUTORS

The British Petroleum Co., Ltd. (England)  
 E. I. DuPont DeNemours & Company  
 The Lilly Research Laboratories, Eli Lilly & Co.  
 The NMR Discussion Group of the U.K.  
 The Perkin-Elmer Company  
 Pfizer, Inc.  
 The Procter & Gamble Co., Miami Valley Labs  
 Programmed Test Sources, Inc.  
 Union Carbide Corporation  
 Xerox Corp., Webster Research Center

DEADLINE DATES: No. 243: 4 December 1978  
 No. 244: 8 January 1979

All Newsletter Correspondence, Etc. Should Be Addressed To:

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

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 242

Ali, A. A. M. .... 28  
 Cancellieri, G. .... 13  
 Cavalli, L. .... 13  
 Cooper, J. W. .... 31  
 Crooks, L. .... 5  
 Dalton, D. R. .... 23  
 Elgert, K. F. .... 1  
 Formacek, V. .... 7  
 Garroway, A. N. .... 6  
 Harris, R. K. .... 28  
 Highet, R. J. .... 16  
 Kosfeld, R. .... 1  
 Kramer, G. W. .... 3  
 Kubeczka, K. H. .... 7

Lanzini, L. .... 13  
 Laszlo, P. .... 18  
 Lauterbur, P. C. .... 12  
 Levy, G. C. .... 11  
 McCain, D. C. .... 3  
 Maciel, G. E. .... 20  
 Moniz, W. B. .... 6  
 Patt, S. L. .... 26  
 Poranski, C. F. .... 6  
 Resing, H. A. .... 6  
 Robinson, C. H. .... 16  
 Roth, K. .... 21  
 Santini, R. E. .... 3  
 Santini, R. E. .... 33

# For those who expect more in FT NMR Spectrometers ... it's JEOL



## The FX60Q, FX90Q & FX100 Feature:

- (DQD) DIGITAL Quadrature Detection System
- Multi-Frequency TUNEABLE Probe observation
- Dual Frequency probes
- 4-channel DIGITAL phase shifters (DPS)
- Comprehensive auto-stacking system
- Foreground/Background system
- Computer based pulse programmer with Multiple Pulse Sequence Generator
- CPU Expandable to 65K words (MOS)
- 2-channel 12 bit AD/DA
- $T_1\rho$ /spin locking system
- Disc storage systems
- Multi-Mode HOMO/HETERO decoupling capabilities
- Programmable Variable Temperature Unit
- Simplex Y/Curvature gradient controller

Prof. Dr. R. Kosfeld  
Physikalische Chemie  
Universität Duisburg

D-4100 Duisburg, 09.10.1978  
Bismarckstraße 90  
Telefon: 0203/392319/320

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

TX 77843 USA

### $^{13}\text{C}$ -NMR-Spectroscopy of Poly(vinyl chloride)

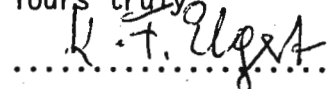
Dear Barry,

$^{13}\text{C}$ -NMR-Spectroscopy has been applied very successful to the determination of monomer sequences in poly(vinyl chloride)<sup>1, 2, 3, 4</sup>. Normally, spectroscopic investigations are performed in o-dichlorobenzene at 150 °C, which is near the thermal degradation of the polymer. We analyzed  $^{13}\text{C}$ -NMR-Spectra of PVC at 65 °C in o-dichlorobenzene, tetrahydrofurane, 1,2-dichloroethane, dimethylformamide, dimethylsulfoxide, nitrobenzene, cyclohexanone, butanone-2 and dimethylacetamide (10% w/v, DMSO- $\text{d}_6$  as an external lock and reference, 500 scans,  $t_p=12 \mu\text{sec}$ , 16k fib<sub>7</sub>). The polymer solutions have been prepared 2-3 days before at 100 °C.

We observed 10 distinct spectra with different numbers of observable resonance lines. Four spectra are shown in fig. 1-4. The sample under study is characterized by  $m=r=0,5$ . We explain our results by a specific influence of the solvent on the populations of the chain conformers. Corresponding calculations including the assignment have been started and will be reported at a later time. From a more practical view point it is recommended to lower the temperature and to change the solvent in order to observe the resonance lines of all possible configurational sequences.

We thank Dr. W. Hull from BRUKER-PHYSIK in Karlsruhe (West-Germany) for measuring the spectra on his WH 270.

Best regards,  
Yours truly



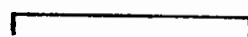
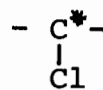
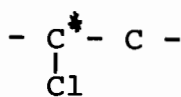
(K.-F. Elgert)

  
(R. Kosfeld)

#### References (not complete):

1. J. Schaefer, *Macromolecules*, 2, 210 (1969)
2. Y. Inoue, I. Ando, A. Nishioka, *Polym. J.*, 3, 246 (1972)
3. C.J. Carman, *Macromolecules*, 6, 725 (1973)
4. I. Ando, Y. Kato, A. Nishioka, *Makromol. Chem.*, 177, 2759 (1976)

$^{13}\text{C}$  NMR Spectra  
of PVC, 65 °C



2 ppm

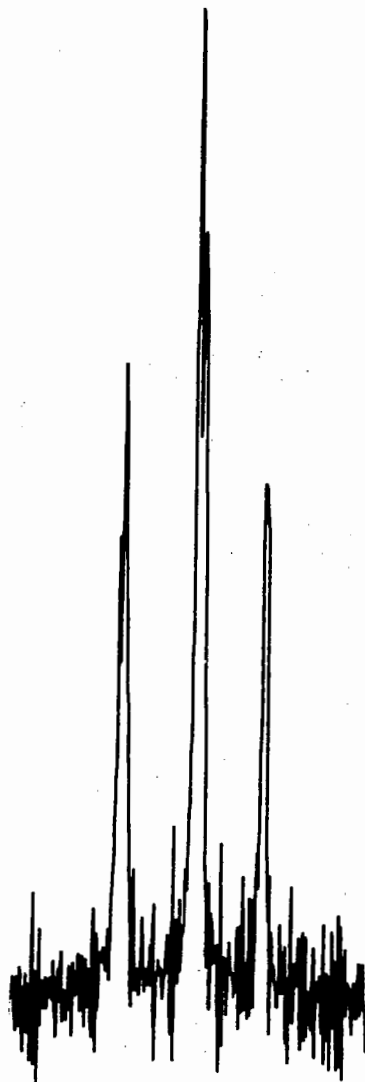


Fig.1

Solvent: DMSO

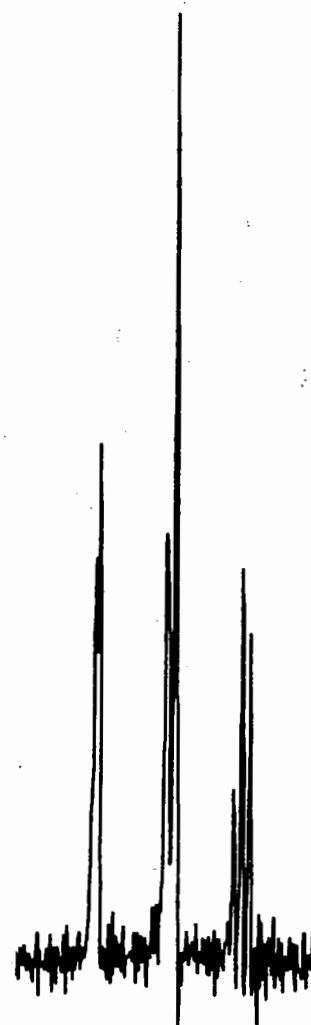


Fig.3

Solvent: 1,2-dichloroethane

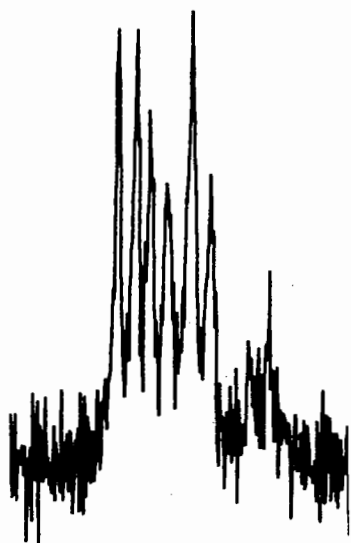


Fig.2

Solvent: DMSO

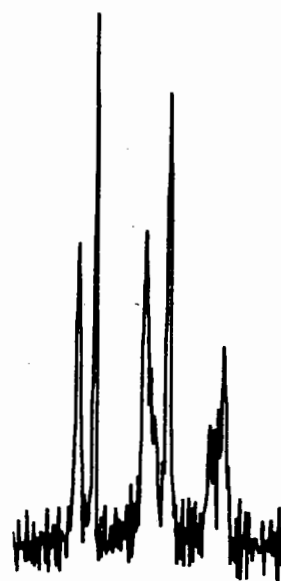


Fig.4

Solvent: 1,2-dichloroethane



## PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

CHEMISTRY BUILDING

WEST LAFAYETTE, INDIANA 47907

October 11, 1978

Barry Shapiro  
Texas A and M University  
College of Science  
College Station, Texas 77843

Title: Diffusion of ambient helium into NMR probe dewars.

Dear Barry:

Please credit this contribution to the subscription of Dr. N. Muller at Purdue.

We would like to report on an unusual and unrecognized problem associated with low-level ambient helium in the laboratory atmosphere and the failure of high field NMR probes. During the installation of our high field NMR facility we observed a sudden loss in S/N of our 150 MHz probes during heteronuclear decoupling. After careful analysis we concluded that the probe was arcing, but the effect could not be demonstrated outside the magnetic field. A lucky observation that the probe was glowing inside the magnet bore was the key to this problem.

It was finally determined that the dewar (inside the NMR probe) was acting as a gas discharge tube. This discharge was identified as due to helium by setting up a periscope in the magnet bore and directing the resultant light to a simple spectroscopic device. We were able to identify all of the tabulated emission lines for helium in the visible range, but no other emission lines or continuum were observed. Clearly helium associated with the operation of our solenoids had diffused into the dewars in the probe. The magnetic field increased the collision probability of helium ions formed by the decoupler fields to the point that a discharge could be sustained.

This result was surprising to us, but later we experienced similar problems with other probes. A search of the literature has revealed that this effect is well known in the electronics industry. Apparently quartz is very permeable to helium and its use is avoided in the construction of modern microwave and other electronic tubes. There are indications that pyrex and some other glasses would be substantially better in this respect.

I would like to emphasize that this failure mode will occur in any dewar made of quartz in an ambient environment where helium is present. For this reason the failure mode will be independent of the manufacture of the NMR system.

Our immediate preventative measures include venting helium to the outside and storing the probes away from the helium enriched atmosphere. Strangely enough, a probe which is already positioned in the bore is well protected by its cooling air column and will not exhibit this effect. The operative factor is definitely associated with exposure during storage of the probes.

This problem is of particular interest to those who use helium as a spinner drive gas in cross polarization studies. The general user would appear likely

to encounter the problem when a superconducting system is installed or if a conventional electromagnet system is operated in the vicinity of a superconducting spectrometer.

We are pursuing a solution to this problem and will be happy to answer any questions which might occur to the interested reader.

Yours,

*Robert E. Santini*

Robert E. Santini

*Gary W. Kramer*

Gary W. Kramer

Doug C. McCain

*Douglas McCain*

RES:mm

---

CONT'D. FROM P. 5

An opening exists for a person to develop image processing programs. Programming ability should include FORTRAN and MACRO 11, preferably under an RT11 monitor. Programs to be developed are a phase and amplitude correction for scan lines, a graphics display of an array of scan lines and a picture processing system for the two dimensional pictures. Familiarity with the processing of NMR spectra is desirable but not necessary. Applicant should have a Masters Degree, or a Bachelors Degree and one year experience.

The University of California, San Francisco, is an Equal Opportunity/Affirmative Action Employer. Women and minorities are encouraged to apply. Interested applicants should contact Lawrence Crooks (415) 952-1369.

## UNIVERSITY OF CALIFORNIA, SAN FRANCISCO

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



SANTA BARBARA • SANTA CRUZ

SCHOOL OF MEDICINE  
DEPARTMENT OF RADIOLOGY  
EXPERIMENTAL NUCLEAR INSTRUMENTATION

UCSF Radiologic Imaging Laboratory  
400 Grandview Drive  
South San Francisco, California 94080  
(415) 952-1366

October 23, 1978

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

The Department of Radiology at UCSF, School of Medicine, is looking for personnel to work on a nuclear magnetic resonance imaging system. The project goal is to develop an NMR system capable of producing images of proton density and T<sub>1</sub> of animals. The NMR techniques used are multi-dimensional Fourier Transform NMR, pulsed gradients and selective irradiation. Both academic and non-academic positions are available for this grant-supported research.

An opening exists for a person to plan and perform NMR image scans of live animals. This work will be done in collaboration with M.D.s as a clinical evaluation of NMR images. Experience measuring NMR relaxation times (T<sub>1</sub> and T<sub>2</sub>) is required. Operation of a custom built NMR FT spectrometer will be required to measure the relaxation times of organs inside the animal. Experience with NMR sequences using pulsed gradients is desirable. Familiarity with high resolution spectroscopy is not needed. Applicants should have at least a Bachelors Degree.

An opening exists for a person to supervise the construction and debugging of radio frequency circuits used to produce and amplify NMR signals. The radio frequency system consists of a frequency synthesizer, transmitter, sample coil, receiver and demodulator. The range of frequencies involved is 1 to 50 MHz. Experience with the design of RF circuits in this frequency range or with NMR spectrometers is required. Applicants should have at least a Bachelors Degree.

CONT'D. BOTTOM OF P. 4





# NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20375

IN REPLY REFER TO:

6170-544:HAR:blr

25 October 1978

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

Dear Dr. Shapiro:

Postdoctoral fellowships tenable at the Naval Research Laboratory are awarded annually through a competition under the auspices of the National Research Council. There are 15-20 of these throughout NRL awarded annually at a stipend of about \$19 K; renewal for a second year is often made. Applicants must be citizens of the United States. As the complete application must be in the hands of NRC by January 15th, and as the competition is great, prospective applicants are advised to begin preparation of proposals, etc. as soon as possible. Materials may be obtained from the NRL or from the undersigned.

The most recent and vigorous development at NRL is that of proton enhanced  $^{13}\text{C}$  NMR. Two spectrometers are available: a) a liquid state double resonance spectrometer which uses the J coupling to polarize the nuclei, and b) a solid state  $^{13}\text{C}$  spectrometer with magic angle spinning. Multinuclear capabilities are available for high resolution and solid state relaxation studies. An EPR spectrometer is also available.

Current interests include: a) analysis, mechanical properties and other basic studies of structural polymers; b) theory of the cross polarization experiment; c) electroactive materials, e.g. (SN) $_x$ , polyacetylene and graphites; and the analysis of molecules chemisorbed on surfaces. We invite letters of inquiry which outline the applicants interests.

Sincerely,

*Bill Moniz* *Al Garroway* *Chester F. Poranski*

William B. Moniz, Allen N. Garroway and Chester F. Poranski  
Code 6110  
(polymers and theory)

*Henry A. Resing*  
Henry A. Resing  
Code 6170

(electroactive polymers, graphites, and surfaces)

# BRUKER ANALYTISCHE MESSTECHNIK GMBH

Brüker Analytische Meßtechnik GmbH · Silberstreifen · D-7512 Rheinstetten-Fo

Professor Barry L. Shapiro  
Department of Chemistry  
Texas A + M University  
College Station, Texas 77843  
USA

Telefon (0721) 5 1185-89  
Telex (07) 826836

Westfalen-Bank AG Düsseldorf  
Nr. 4110013 BLZ 300 200 00

BfG Karlsruhe  
Nr. 10 774 422 00 BLZ 660 101 11

Dresdner Bank Karlsruhe  
Nr. 562 116100 BLZ 660 800 52

Postscheckkonto Karlsruhe  
Nr. 1375 91-752 BLZ 660 100 75

*Geschäftsbereiche*  
*Kernresonanz*  
*Elektronenresonanz*  
*Infrarot*  
*Polarographie*  
*Magnetsysteme*  
*Elektronische Geräte*  
*Computerbau*



Ihr Zeichen

Ihre Nachricht vom

Unser Zeichen

Datum  
September 5, 1978

Dear Professor Shapiro:

$^{13}\text{C}$  spectroscopy appears to be a useful tool for qualitative and with certain limitations quantitative analyse of the essential oils.

These oils, important for the food industry are mixtures of a wide variety of substances, mostly mono- and sesquiterpenes. A generally common method for analysis of the essential oils is gas chromatography which despite good sensitivity has certain disadvantages:

- 1) thermal instability of the components,
- 2) instability catalysed by column materials,
- 3) same retention times for substances of diverse chemical structure (for example 1,8-cineolXbeta-phellandrene),
- 4) impossibility to detect non-volatile substances.

$^{13}\text{C}$  NMR spectroscopy has the following advantages:

- 1) is non-destructive
- 2) fast determination of main components,
- 3) direct information about the structure of unknown components,
- 4) gives information of the total mixture including non-volatile components.

As illustration we present data for two peppermint oils: from two different plants: Mentha arvensis and Mentha piperita. The presence of menthofuran in the mentha oils is undesirable and influences the price of the product. The determination of methofuran at levels as low as 5 % is accomplished using  $^{13}\text{C}$ -NMR in a few minutes. In the spectrum of Mentha piperita oil are the most characteristic signals of menthofuran (at 150.53; 137,21;

Blatt

zum Schreiben vom

BRUKER ANALYTISCHE MESSTECHNIK GMBH

Sept. 5, 1978

119.25, 117.31 and 7.94 ppm) indicated by x.

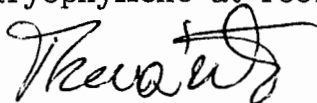
The figure shows 20.1 MHz  $^{13}\text{C}$ -NMR spectra for the two oils mentioned above. The sample contains the oil as isolated plus 10 %  $\text{C}_6\text{D}_6$  (128.0 ppm) in a 10 mm tube. Spectral width 4700 Hz/32K data points, flip angle  $25^\circ$ , acquisition time 3.6 sec., BB decoupling 2 watts; exponential linebroadening 0.15 Hz, 11 000 scans.

The table shows the quantitative analysis for assigned components representing at least 98 % of the total constituents. The correspondence with GC data is excellent.

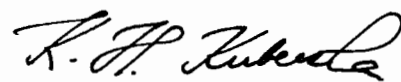
A complete analysis of 60 oils is in preparation for publication. Interested readers should contact V. Formacek for more information.

Substance	% in M. piperita	% in M. arvensis
Menthol	45.4	32.8
neo-Menthol	3.8	4.9
Menthone	20.6	29.5
iso-Menthone	3.7	9.4
Menthylacetate	4.8	1.4
Pulegone	2.6	3.3
Piperitone	0.6	2.3
Carvone	0.5	1.9
alpha-Pinene	0.5	1.6
beta-Pinene	1.0	1.9
Limonene	2.4	5.1
Sabinene	0.3	0.3
1,8-Cineole	6.0	-
Menthofuran	5.5	-
Octanol-3	-	3.8
Myrcene	0.3	0.7
Germacrene D	0.5	0.3
Caryophyllene	traces <sup>x)</sup>	traces <sup>x)</sup>

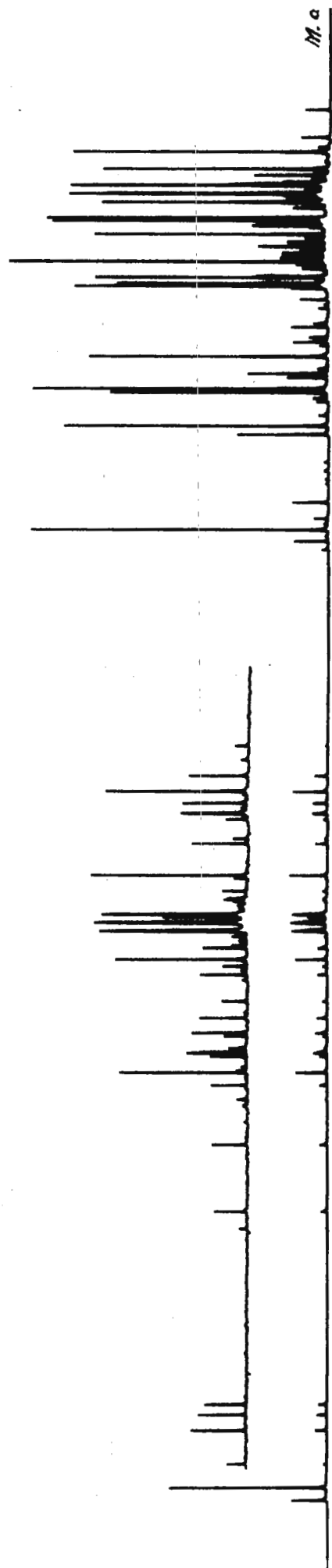
x) GC value for caryophyllene are higher due to the coalescence of caryophyllene at room temp. at 20.1 MHz.



V. Formacek  
Bruker Analytische Messtechnik GMBH



Prof. Dr. K.H. Kubeczka  
University Würzburg







# DATA SYSTEMS

## ASPECT 2000



The ASPECT 2000 is a complete data acquisition and processing system which can be used efficiently wherever the time dependence of physical observables must be stored and analyzed. It is a high performance mini-computer with dual-input A/D converter, D/A converters and numerous interfaces. Together with its comprehensive software, the ASPECT 2000 offers unmatched capabilities for data-collection, calculation, analysis and output.

- 24-bit word length
- Fast A/D converter:  
250 KHz @ 12-bits
- 2 programmable real-time clocks
- 2 direct-memory-access channels
- 3 arithmetic registers
- 4 index registers for addressing
- 7 vectored interrupt levels
- Fast MOS solid-state memory  
capacity of up to 80 K
- Hardware multiply-divide
- ROM binary tape loader and  
disk bootstrap

The ASPECT 2000 is included as the superior data system in all Bruker high resolution NMR, pulsed NMR, EPR and FT/Infrared spectrometers.

Ideally suited as a general purpose laboratory data system, complete with a wide array of accessories and software.

*Call or Write for Details or a Demonstration*

### BRUKER INSTRUMENTS, INC.

Manning Park  
Billerica, Mass. 01821  
Phone (617) 272-9250

539 Beall Avenue  
Rockville, Maryland 20850  
Phone (301) 762-4440

1801 Page Mill Rd., Suite 212  
Palo Alto, Calif. 94304  
Phone (415) 493-3173

2410 Dunwin Drive, Unit 4  
Mississauga, Ontario, Canada, L5L 1J9  
Phone (416) 625-2374

Department of Chemistry

The Florida State University  
Tallahassee, Florida 32306

October 31, 1978

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

Postdoctoral Openings in NMR at Florida State University

Dear Barry:

Our NMR Research group once again has a number of postdoctoral openings which are described immediately below:

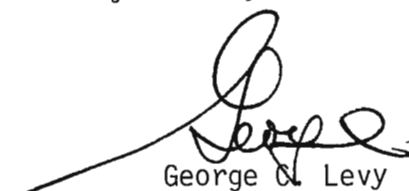
1. Physical or Polymer Chemist with interest in  $^{13}\text{C}$  and other nuclei NMR of synthetic polymers (joint postdoctoral with Leo Mandelkern and with me). This work will include liquid and solid phase nmr. Both of our supercon spectrometers will be used.
2. Inorganic or Physical Chemist to use metal ion nmr to evaluate solution chemistry of lanthanides and other metals. Inorganic and bio-inorganic applications (joint position with Gregory Choppin).
3. NMR Spectroscopist, or digital hardware-oriented person to work on new computer methods (laboratory data networking, etc.) and, perhaps, continuing nmr instrumentation developments.

Each of these positions involves a broad range of new techniques, using our Bruker HX-270 and SEMINOLE spectrometers. Salaries range from \$9,700 depending on experience; a higher salary is available for the computer project.

I will be most happy to consider outstanding applicants in organic chemistry or any other discipline for these or other projects underway.

All interested candidates should write to me and have at least two letters of reference forwarded. Positions 2 and 3 will be available shortly, and should ideally be filled before April, 1979. The position 1 starting date will be after April, 1979.

With warmest regards and 20th Birthday wishes,



George A. Levy  
Professor

GCL:dht

State University of New York  
at Stony Brook  
Stony Brook, New York 11794

Department of Chemistry  
telephone: (516) 246-5050 / 5051

# Stony Brook

November 1, 1978

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

## Postdoctoral Positions Available

Dear Barry:

Several postdoctoral positions will become available in my laboratory during the next several months, all associated in some way or other with NMR zeugmatographic imaging and its medical applications. Individuals with backgrounds in physiology, biochemistry, chemistry, physics and engineering are invited to apply; we are working on all aspects of the problem, including instrument design and construction, new imaging schemes, tissue characterization by relaxation behavior, the distribution and relaxation effects of paramagnetic compounds in organs, animal experimentation and clinical trials.

The State University of New York at Stony Brook is an Equal Opportunity/Affirmative Action employer.

Best regards.

Yours truly,



Paul C. Lauterbur  
Professor of Chemistry

PCL:eg

P.S. We can always use a few more good graduate students, too.

**EUTECO** S.R.A.CASELLA POSTALE 3843 - 20100 MILANO  
TELEFONO: 02 - 64.670 - TELEX: 37111Prof. B.L. Shapiro,  
Texas A & M University  
College of Science,  
Dpt. of Chemistry  
College Station,  
TEXAS 77843

U. S. A.

Paderno D., 21/09/78

48/SEAN

Subject : hydrolysis of propylene oxide

Dear Prof. Shapiro,

we recently completed a NMR study of the hydrolysis of propylene oxide to propylene glycol, the results of which we want to summarize here for those who can be interested. The reaction has been studied at ca. 3 % in aqueous solution ( $D_2O$ ) with ca. 6 % of NaCl at different pH values (6 + 13) and in a range of temperatures (25 + 90°C). The pH values were adjusted with NaOH 1 N solution. The measurements were performed at 60 MHz with a Jeol JNM-C-60 HL spectrometer, using sealed NMR tubes.  $CH_3COONa$  was added as internal standard to get quantitative data. A typical NMR spectrum of the reaction mixture is shown in the attached figure. The  $CH_3$  doublets of the propylene oxide and of the propylene glycol are shown at  $\delta = 1.33$  and  $\delta = 1.15$  respectively. The  $CH_3$  group of the internal standard is at  $\delta = 1.97$ . The concentration of the propylene oxide (PO) follows a 1° order kinetic :

$$\ln PO = -Kt + \ln OP^0$$

All our results can be rationalized with the hypothesis of the existence of two reactions, one uncatalysed and the other one



EUTECO...

catalysed by the  $\text{OH}^{\ominus}$  ions.

At 60°C we obtained :

$$K = K_0 + K_{\text{OH}} [\text{OH}]$$

$$\text{with } K_0 = \text{ca. } 0.2 \cdot 10^{-4} \text{ sec.}^{-1}$$

$$10^3 K_{\text{OH}} = -0.031 + 6.6 [\text{OH}]$$

The activation parameters of the hydrolysis reaction at three different pH values were found as follows :

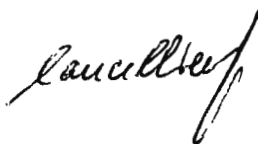
pH	log A	$E_a$ (Kcal/m)	$\Delta H^*$ (Kcal/m)	$\Delta S^*$ (cal/grade)
ca. 8	5.496	15.34	18.25	-25.6
12	6.832	16.85	16.2	-29.4
13	7.525	16.44	15.8	-26.2

yours sincerely,

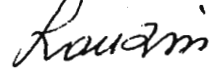
L. Cavalli



G. Cancellieri



L. Lanzini



**EUTECO S.p.A.**

Centro Ricerche

v. Reali, 4

20037 Paderno D. (MI)

ITALY

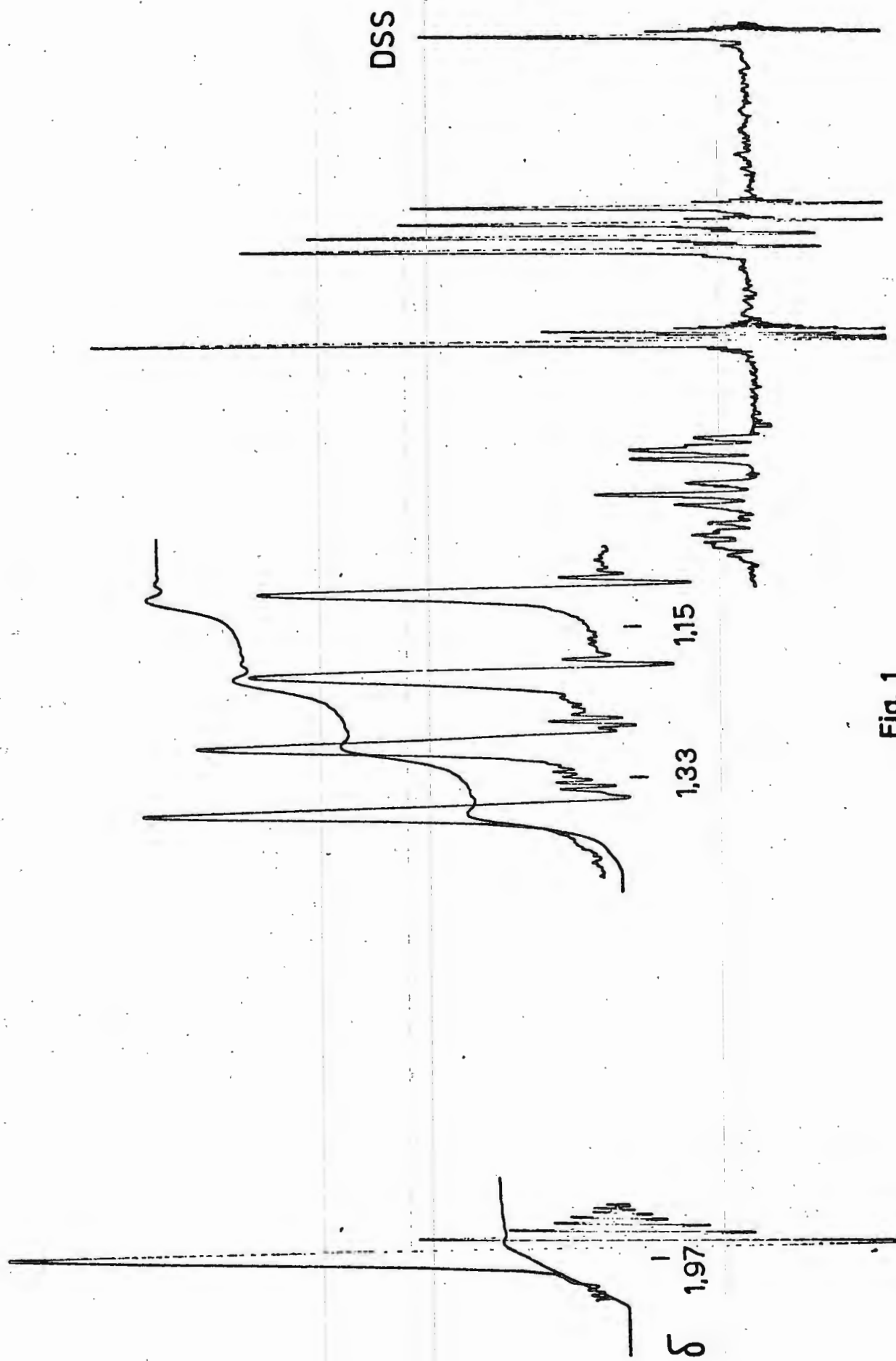


Fig. 1



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
PUBLIC HEALTH SERVICE  
NATIONAL INSTITUTES OF HEALTH  
BETHESDA, MARYLAND 20014

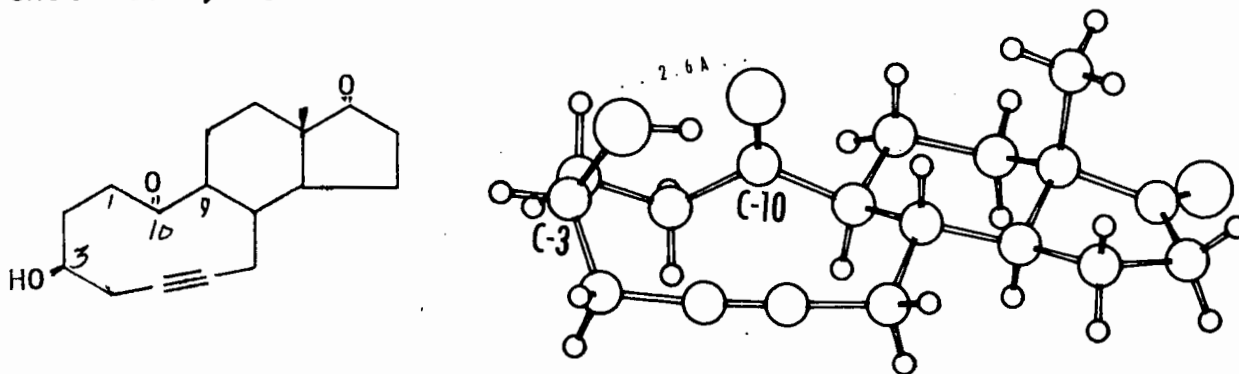
242-16

NATIONAL HEART, LUNG, AND BLOOD INSTITUTE  
25 October 1978

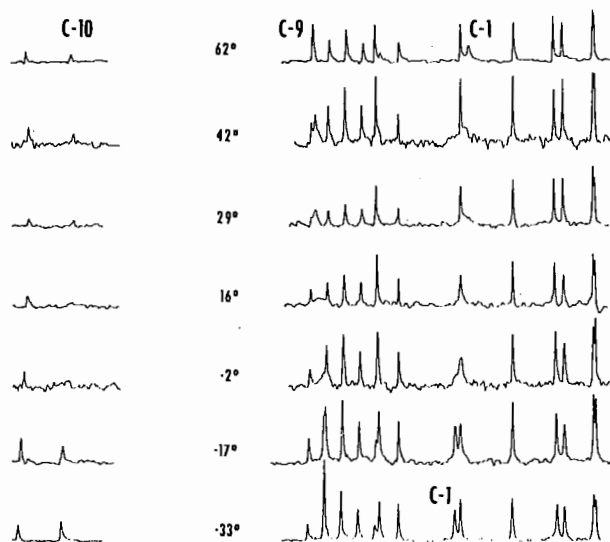
Prof. B. L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843

Dear Barry,

We have studied a series of secosteroids, such as that below, because of their interest as substrates or



suicide inactivators of steroid transforming enzymes. The C-13 spectrum of this hydroxydiketone shows C-1 quite broad at room temperature. Chilling to 15° produces broad peaks for



C-1, 9 and 10, the other carbons remaining unaffected, even at substantially lower temperatures. This specificity seems somewhat surprising because models suggest that the large ring should be quite floppy.

Our current interpretation postulates a role for an intramolecular hydrogen bond between the C-3 hydroxy group and the C-10 ketone. The speculative conformation drawn above, based on that observed in crystal studies of the corresponding triketone, shows an encouraging 0.0 distance of 2.6 Å. Addition of a small amount of dimethylsulfoxide to the methylene chloride solution, to disrupt the intramolecular hydrogen bond, alters the chemical shifts of most of the carbon atoms of the large ring, while those of the C and D rings are unchanged. The C-10 carbonyl is shifted upfield, consistent with the hydrogen bond having produced the anticipated downfield shift.

The infrared spectra of the material are even more striking. That in methylene chloride shows OH-stretching at  $3520\text{ cm}^{-1}$ , suitable for an intramolecular hydrogen bond, with the carbonyl of C-10 split into a doublet ( $1705, 1692\text{ cm}^{-1}$ ); that in tetrahydrofuran shows only an intermolecular hydrogen bond ( $3360\text{ cm}^{-1}$ ) with the carbonyl as a single peak at  $1700\text{ cm}^{-1}$ .



C. H. Robinson  
Department of Pharmacology  
Johns Hopkins University  
Baltimore, Maryland

Yours very truly,



R. J. Highet  
Laboratory of Chemistry

---

CONT'D. FROM P. 18

Gramicidin A, also a linear antibiotic, a pentadecapeptide 4, confers ionic permeability on membranes : 4 forms channel-like dimers across which univalent ions are invited to swim. A recent model for the gramicidin A channel infers from conductance data a specific cationic binding site at each entrance to the channel. We looked at the influence on the relaxation rates of a change in Larmor frequency from 23.80 to 62.86 MHz. Indeed, we find in ethanol-water mixtures (90:10) the dimeric antibiotic to bind  $\text{Na}^+$  cations at well-defined sites, with a binding constant  $K = 4\text{ M}^{-1}$  (at 309 K). Partial desolvation of  $\text{Na}^+$  occurs upon binding, from the relatively high magnitude of the quadrupolar coupling constant for bound sodium (1.7 MHz). The binding sites are identified with the outer sites flanking the channel entrances. The rate constants for binding and release are  $k_+ \leq 2.2 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$  and  $k_- \leq 5.5 \times 10^8\text{ s}^{-1}$ .

These studies have been carried out in collaboration with Drs. J. Grandjean (1 and 3), C. Coibion (2), and A. Cornélis (4).

With kindest regards,

Cordially yours,



Pierre Laszlo



Professeur PIERRE LASZLO

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

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

October 10, 1978

A Grab-Bag of Grabbers.

Dear Barry,

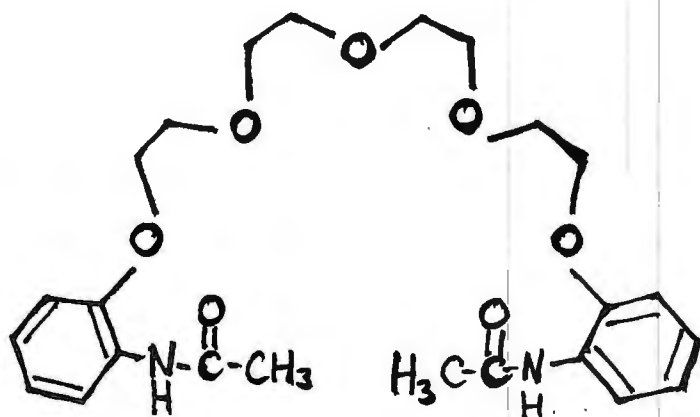
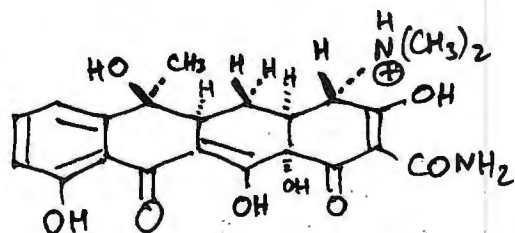
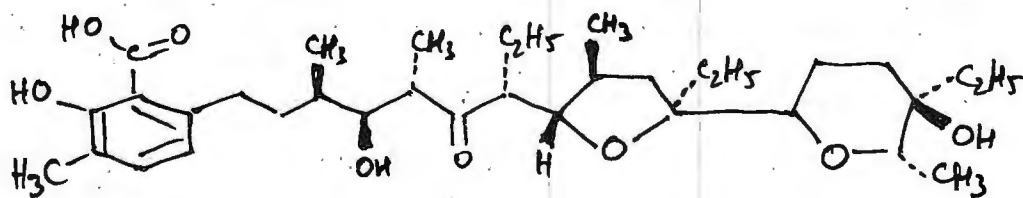
Since my paean of last year (TAMU-NMR 230-30), sodium-23 mmr has continued to reward handsomely our relentless efforts. We have acquired a Bruker WP-80 spectrometer to supplement the HFX-90, so that machine time is no longer a problem for my group. Molecular ion-grabbers go by the scholarly name of ionophores, and we have played with a few of those.

We have looked at the interaction of  $\text{NaClO}_4$  with the open crown ether 1, synthesized by Fritz Vögtle and Heinz Sieger, of the University of Bonn. A strong complex forms in pyridine solution with  $K_f = 10 \cdot 10^3$  in the 50-5°C temperature range, corresponding to  $\Delta H_f^\circ = -17 \text{ kcal.mol}^{-1}$  and  $\Delta S_f^\circ = -48 \text{ cal.mol}^{-1} \cdot \text{K}^{-1}$ . We interpret the strongly negative entropy term as evidence for a cyclical structure in the complex: the presence of the alkali metal cation induces wrapping of the polyether chain around it.

Going to natural products, we examined the complexing abilities of the antibiotic ionophores tetracyclin 2, lasalocid (X-537 A) 3, and gramicidin A 4. In aqueous solution at pH 8.6, we determined for 2 the binding constants not only for the sodium, but also, through competition experiments, for the other alkali metal cations. The dissociation constants for 1:1 complexes are of the order of 50 mM, and they follow the sequence:  $\text{Li}^+ < \text{Na}^+, \text{Cs} < \text{K}^+ < \text{Rb}^+$ .

Lasalocid 3 is a hungry fellow: not only does it complex and transport across membranes ions of a wide variety (alkaline, alkaline earth, rare earth, transition metal ions), it also effects complexation of biogenic amines and their distribution across the membrane (see *inter alia* the handsome mmr work of Shen and Patel, and of Degani and Friedman). We find, in methanol-n-hexane mixture (28:72 v/v), *competitive* binding to 3 of  $\text{Na}^+$  and biogenic amines such as serotonin, 3-hydroxytyramine, and (L)-norepinephrine, with binding constants between 150 and 250  $\text{M}^{-1}$  (at 297-299 K), *i.e.* close to that for  $\text{Na}^+$  at the same temperature (ca. 300  $\text{M}^{-1}$ ), in this medium chosen to mimic the polarity at the membrane-water interface.

CONT'D. BOTTOM OF P. 17

1  
~2  
~3  
~

4  $\equiv$  formyl-L-Val-Gly-L-Ala-D-Leu-L-Ala-D-Val-L-Val-D-Val-  
(L-Trp-D-Leu)<sub>3</sub>-L-Trp-ethanolamide.



1(303)491-6480

Colorado State University  
Fort Collins, Colorado  
80523

Department of Chemistry

October 17, 1978

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

Laboratory Manager Position Available for Regional NMR Center

Dear Barry:

The NSF-funded NMR Center at Colorado State University, which will be based mainly on two superconducting nmr spectrometers, is seeking highly qualified applicants for the position of laboratory manager, at a starting annual salary of \$21,000 to \$24,000. Candidate must have a Ph.D. in chemistry or equivalent degree and extensive experience and demonstrated productivity in nmr applications and should have demonstrated abilities for management. Duties include providing nmr service, consultation and collaboration, and day-to-day administration of the Center, including direct supervision of two other technical staff members. Applications, including curriculum vitae and bibliography, and three letters of recommendation should be sent to Professor G.E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Application deadline is December 15, 1978. Starting date is Jan. 1 - Feb. 1, 1979. COLORADO STATE UNIVERSITY IS EEO/TITLE IX EMPLOYER. EQUAL OPPORTUNITY OFFICE: 314 Student Services Building.

Sincerely,

Gary E. Maciel  
Professor and

Director of the Regional NMR Center

1b

FREIE UNIVERSITÄT BERLIN

Fachbereich Chemie (FB 21)  
Institut für Organische Chemie (WE 02)

FU

BERLIN

Dr.K.Roth

Freie Universität Berlin,  
FB 21, WE 02, Takustraße 3, 1000 Berlin 33

10-18-78

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

Title: Selective Measurement of Coupling Constants between Quaternary  
Carbons and Phosphorus

Dear Prof.Shapiro:

Recently we have shown <sup>1)</sup> that the off-resonance noise decoupling technique results in spectral information for signal assignments. In the  $^{13}\text{C}\{^1\text{H}\}$  case only the signals of the tertiary and primary carbons will be broadened while the signals of the quaternary carbons ( and the antisymmetric transition in simple  $A_2X$  cases) stay sharp and allow a simple identification <sup>2)</sup>.

This is not only valid for simple spin systems but also for carbons which are further splitted by couplings to hetero atoms. The benefits of this technique is demonstrated with fluorenyliden-triphenylphosphorane.

When a suitable  $H_2$ -field is applied the signals of the quaternary carbons are broadened ( $\Delta\nu_{1/2} \approx 50$  Hz) and the sharp lines of the quaternary carbons and their hetero coupling constants can be easily measured.

1) K.Roth,Org.Magn.Reson. 10,56(1977)

2) Allerhand et al. Biochemistry 12,1335(1973)

Sincerely Yours





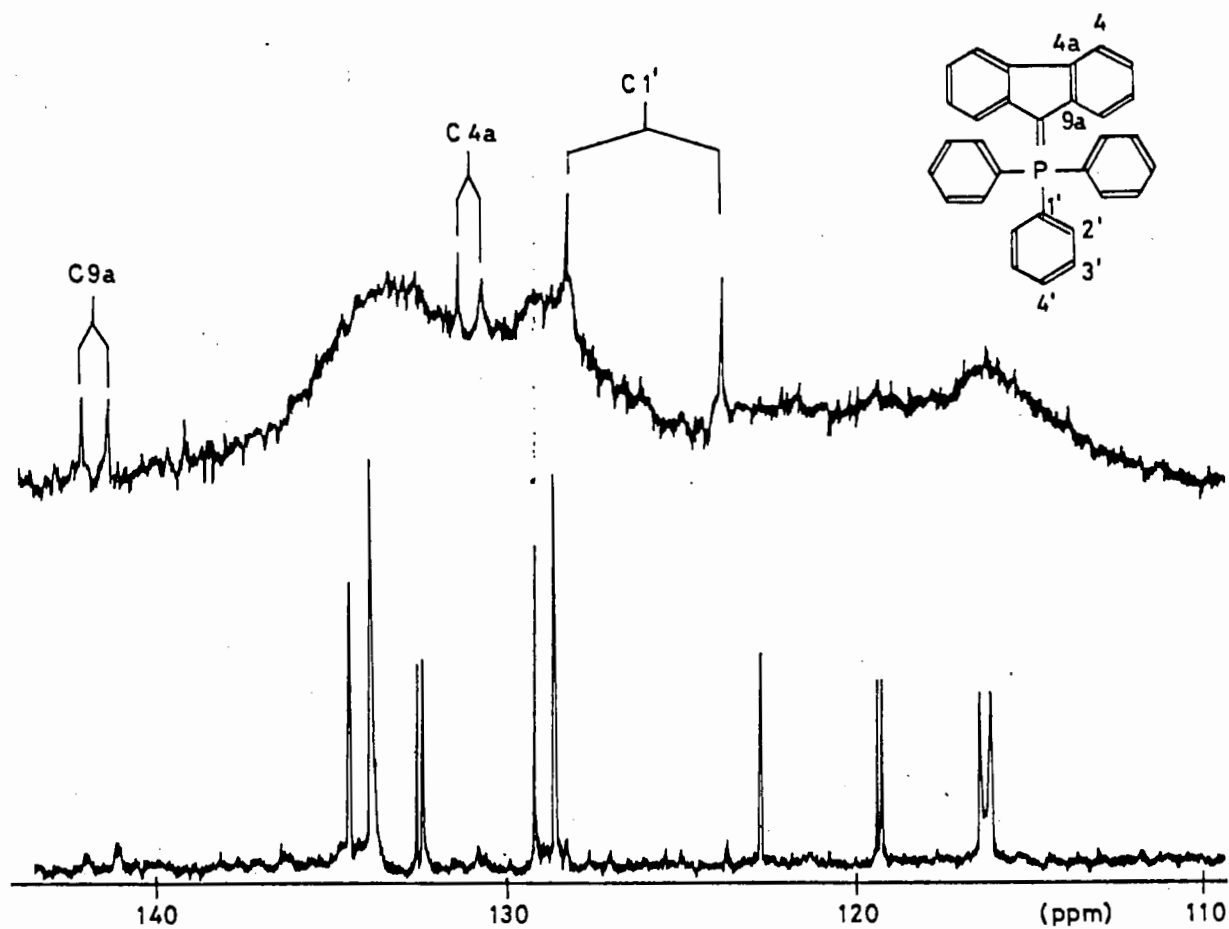


fig. Aromatic region of the carbon spectra (20 MHz) exp.conditions:  
 aquisition time 1 s , pulse delay 2 s , noise bandwidth 500 Hz,  
 $J_{\text{H}_2} \approx 4500$  Hz  
 top 84,000 pulses,  $^1\text{H}$  off-res.noise decoupled, dec.offset -46 ppm  
 6,000 pulses,  $^1\text{H}$ .noise decouplde, dec.offset +7 ppm.



TEMPLE UNIVERSITY  
COLLEGE OF LIBERAL ARTS  
PHILADELPHIA, PENNSYLVANIA 19122

DEPARTMENT OF CHEMISTRY

16 October 1978

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

Dear Barry,

Temple University of the Commonwealth System of Higher Education has an opening for an NMR technician.

The successful candidate will be expected to service our PE 90 MHz equipment which is used for routine spectra as well as to maintain and develop our Nicolet 1180 equipped multinuclear Varian XL-100-15 facility. This will require close work with faculty and graduate students. We also expect that the individual hired will wish to devote some time to his or her own problems and we will actively support such an effort.

Salary will be commensurate with experience and, of course, will include the fringe benefits of a large urban University.

Interested applicants should forward, as soon as possible, their curriculum vitae and a statement of their availability. Temple University of the Commonwealth System of Higher Education is an affirmative action/equal opportunity employer. If more detailed information is needed, I can be reached by telephone at (215) 787-7138.

Sincerely,

David R. Dalton  
Professor of Chemistry

DRD:w



# A hot performer at a cool 4.2°K



## Varian introduces: The XL-200 superconducting FT NMR spectrometer

In a cost- and resource-conscious world, the new XL-200 with 47-kG superconducting magnet makes a lot of sense. To begin with, its high-field performance and advanced design come in a truly affordable package. And economy characterizes the XL-200 spectrometer in other ways, too—such as the low-loss dewar unit, which lets the system operate over three months on only 25 liters of liquid helium!

The basic instrument is designed for  $^1\text{H}$  (200 MHz) and  $^{13}\text{C}$  (50.3 MHz) observation, but it will accommodate a host of other nuclei with the optional 20-80 MHz broadband accessory.

The XL-200's data management system tops all conventional concepts of versatility and convenience. There are two processing units working in tandem—one 32 bits wide and very fast for data acquisition, the other programmed in a high-level language and extremely flexible for data manipulation. Both operate continuously and, together with the XL-200's full complement of built-in I/O devices, offer you unique multi-tasking capability and high sample throughput.

And that's only the beginning of a long list of features which could read like your own NMR wishlist:

- 47-kG Nb-Ti superconducting magnet with 50-mm bore
- 25 liters liquid He dewar capacity; 3-month refill interval
- 35 liters liquid  $\text{N}_2$  dewar capacity; 14-day refill

- interval (45 days with optional refrigerator)
- 5- and 10-mm samples standard; other sample sizes optional
- Broadband probes covering 20-80 MHz and 188-212-MHz ranges
- Flexible mix/match RF system with fixed-frequency sources such as  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$
- Compatible with RF synthesizer for broadband multi-nuclear operation
- 50-kHz spectral widths with quadrature phase detection
- Automatic  $^2\text{H}$  internal field/frequency stabilization with exclusive AutoLock™ circuit
- $^1\text{H}$  homo/heteronuclear decoupler for a wide variety of gated modes
- Programmable 32K CPU for data processing and multi-tasking
- Independent 32-bit parallel processor with dedicated random-access memory for spectrometer control and data acquisition
- Built-in I/O devices include solid-state keyboard; 5M-word moving-head disk with dual platter (one removable); high resolution raster scan storage/display oscilloscope; 32-column line printer; 500 x 240 mm X-Y recorder.

If you would like the balance of the features to compare with your wishlist, write Varian Associates, Inc., Box D-070, 611 Hansen Way, Palo Alto, CA 94303.





# Varian Sales Offices

## **CALIFORNIA**

9901 Paramount Boulevard  
Downey, CA 90240  
Phone: (213) 927-3415

375 Distel Circle  
Los Altos, CA 94022  
Phone: (415) 968-8141

## **COLORADO**

4665 Kipling, Suite 1  
Wheatridge, CO 80033  
Phone: (303) 425-0413

## **GEORGIA**

6650 Powers Ferry Road  
Suite 100  
Atlanta, GA 30339  
Phone: (404) 955-1392

## **ILLINOIS**

205 W. Touhy Avenue  
Park Ridge, IL 60068  
Phone: (312) 825-7772

## **KENTUCKY**

Executive Park, Suite 110  
Louisville, KY 40207  
Phone: (502) 897-0171

## **MARYLAND**

4701 Lydell Drive  
Cheverly, MD 20781  
Phone: (301) 772-3683

## **MASSACHUSETTS**

400 Totten Pond Road  
Waltham, MA 02154  
Phone: (617) 890-8430

## **NEW JERSEY**

25 Hanover Road  
Florham Park, NJ 07932  
Phone: (201) 822-3700

## **NEW YORK**

6489 Ridings Road  
Syracuse, NY 13206  
Phone: (315) 437-6464

## **OHIO**

25000 Euclid Avenue  
Euclid, OH 44117  
Phone: (216) 261-2115

## **TEXAS**

Plaza Southwest  
5750 Bintliff Drive, Suite 202  
Houston, TX 77036  
Phone: (713) 783-1800

## **WASHINGTON**

300 120th Avenue  
Bldg. 2, Suite 230  
Bellevue, WA 98005  
Phone: (206) 454-2910



Instrument Division sales offices and representatives are located in: Algeria, Argentina, Australia, Austria, Benelux, Brazil, Canada, Chile, China, Colombia, Costa Rica, Denmark, Eire, Finland, France, Germany, Great Britain, Greece, Holland, Hong Kong, Iceland, India, Iran, Israel, Italy, Japan, Korea, Lebanon, Malaysia, Mexico, Morocco, New Zealand, Norway, Pakistan, Peru, Philippines, Puerto Rico, Portugal, Scandinavia, South Africa, Spain, Sweden, Switzerland, Thailand, Turkey, United States, Venezuela.

varian / instrument division

25 hanover road / florham park / new jersey 07932

telephone (201) 822-3700



October 30, 1978

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

CRAPS: HOMOSPOIL $T_1$ 'S WITHOUT THE HOMOSPOIL
--

Dear Barry:

In inversion-recovery  $T_1$  measurements, the well-known limitations of homospoil techniques have led to the use of phase-alternation techniques to cancel out the effects of pulse imperfections.<sup>1</sup> It is not commonly realized, but homospoil can be replaced by phase alternation in saturation-recovery experiments<sup>2</sup> as well; phase alternation eliminates the signal induced after the first pulse as well as it eliminates the residual signals induced following the  $180^\circ$  pulse in an inversion-recovery experiment.

Figure 1 demonstrates the use of CAPS (Computer Alternated Phase Sequence) on a  $90^\circ - \tau - 90^\circ$  saturation-recovery experiment. The peak shown is  $^{15}\text{NO}_3$  in doubly enriched ammonium nitrate; the spectra were taken on a Varian FT-80A spectrometer with broadband probe. One "steady-state" FID was discarded at the start of each tau value. A very clean exponential recovery is seen in this "homospoil  $T_1$  without the homospoil."

The true test of such a sequence, however, is for cases in which  $T_1 \approx T_2 \approx T_2^*$ . Under these circumstances, a variety of anomalous signals can accumulate due to signals left at the end of the acquisition time, spin echoes, etc. Figure 2A shows the use of progressive-saturation with CAPS to determine  $^{17}\text{O}$   $T_1$ 's in a sample of acetone and  $\text{D}_2\text{O}$ . Here we see that at short tau values anomalous effects interfere with our ability to measure  $T_1$ 's.

A simple modification, however, corrects this problem. In tribute to the beginning of casino gambling in Atlantic City, I call this technique CRAPS - Computer Rotated and Alternated Phase Sequence. In this experiment, the phase of the first  $90^\circ$  pulse is rotated in phase by  $90^\circ$  every pulse; CAPS is still in use for the second pulse as shown in Table I.

Table I. CRAPS CYCLE

Cycle	First Pulse Phase	Second Pulse Phase	Computer Data Handling
1	$0^\circ$	$0^\circ$	Add
2	$90^\circ$	$180^\circ$	Subtract
3	$180^\circ$	$0^\circ$	Add
4	$270^\circ$	$180^\circ$	Subtract

varian / instrument division

25 hanover road / florham park / new jersey 07932

telephone (201) 822-3700



Figure 2B shows the effect of CRAPS: anomalous effects have been eliminated, and a clean exponential recovery ensues.

Needless to say, the main advantages to saturation-recovery  $T_1$ 's are in studying long  $T_1$ 's. In these cases, the simple CAPS technique is quite sufficient — "homospoil  $T_1$ 's without the homospoil" can be accomplished quite routinely.

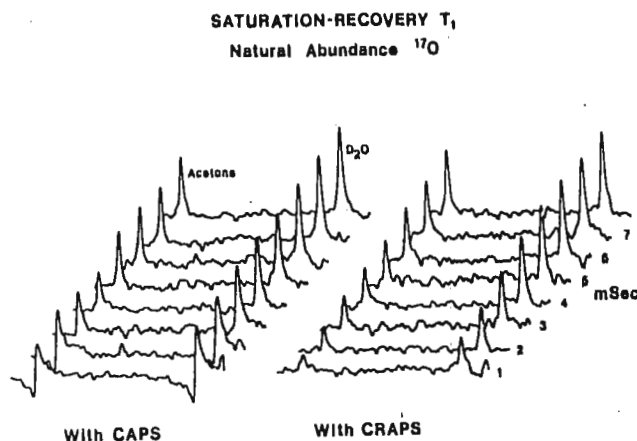
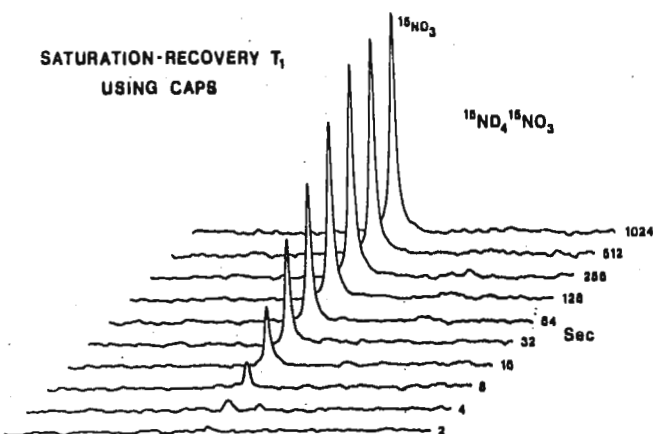
Sincerely,

*Steve Patt*

Steven L. Patt  
NMR Applications Chemist

<sup>1</sup>D.E. Demco et al., J. Mag. Res. 16, 467 (1974).

<sup>2</sup>G. McDonald and J. Leigh, Jr., J. Mag. Res. 9, 358 (1973)





## University of East Anglia

From Dr. R. K. Harris  
Mr. A. A. M. Ali

School of Chemical Sciences  
 University of East Anglia  
 Norwich NR4 7TJ, **ENGLAND**  
 Telephone Norwich (0603) 56161  
 Telegraphic Address UEANOR NORWICH

25th October, 1978

Dear Barry,

TETRAALKYLDIPHOSPHINES; A SPECTROSCOPIC PUZZLE SOLVED

Thank you for your pink letter. The necessary activation energy for writing TAMUNMR Newsletter items seems to increase with the passing years. I think you'll need a multicoloured final reminder to replace the pink one soon.

However, we do have some NMR work to report. For some years we have been interested in tetraalkyldiphosphines<sup>1</sup>. We have been able to stop P-P internal rotation on the NMR timescale only in the case of the tetra-t-butyl compound<sup>2</sup>. Recently, we have examined three other tetraalkyldiphosphines with bulky substituents, viz.  $[\text{Pr}^i\text{Bu}^t\text{P}]_2$  (I),  $[\text{EtBu}^t\text{P}]_2$  (II) and  $[\text{EtPr}^i\text{P}]_2$  (III). Only the racemic form is present in our samples for I and II, but the meso form is also there for III. Some of the results are:-

	I	II	III( <u>racemic</u> )	III( <u>meso</u> )
$\delta_{\text{P}}/\text{ppm}$	15.12	-6.03	-21.40	-17.12
$N_{\text{PC}}(\alpha)/\text{Hz}$	$\begin{Bmatrix} 4.3(\text{Bu}^t) \\ 23.1(\text{Pr}^i) \end{Bmatrix}$	$\begin{Bmatrix} 1.1(\text{Bu}^t) \\ 31.1(\text{Et}) \end{Bmatrix}$	$\begin{Bmatrix} <2.0(\text{Pr}^i) \\ 22.0(\text{Et}) \end{Bmatrix}$	$\begin{Bmatrix} 11.1(\text{Pr}^i) \\ 9.4(\text{Et}) \end{Bmatrix}$

The phosphorus chemical shifts show anomalously low shielding when compared with compounds with smaller alkyl substituents, presumably because the bulky groups are distorting the molecular geometry. The values of  $N_{\text{PC}} \equiv \left| {}^1J_{\text{PC}} + {}^2J_{\text{PPC}} \right|$

for the  $\alpha$ -carbons correlate<sup>3</sup> with the expected position of the alkyl groups with respect to phosphorus lone pairs in the most stable conformation - a group gauche to a lone pair having low values for  $N_{PC}$  while a trans group has a high value.

During this work we used low-power noise decoupling to locate quaternary carbon signals, but were surprised to find sharp signals remaining under these conditions for  $CH_2$  groups in III (see the figure). We showed this spectrum, shortly after we obtained it, as a "spectroscopic puzzle" at the international meeting in Banff in 1977, asking for explanations but getting no satisfactory ones. However, the matter is actually simple, as discussed by Roth<sup>4</sup> for the related case of off-resonance decoupling. The fact is that when the  $CH_2$  protons are considered on a "composite particle" basis, the S state acts as if the protons were non-magnetic. The corresponding carbons therefore require no proton decoupling except from more distant protons. They therefore behave like quaternary carbons, but since the S state has only a quarter of the total spin population, the sharp signals seen in the figure have only a quarter of the fully noise-decoupled signal; they may thus be distinguished from signals due to quaternary carbons, as well as from CH and  $CH_3$  groups.

Our TAMUNMR duty is fulfilled for another year, we hope.

With best wishes,

Yours sincerely,

*Robin*

R. K. Harris

*Ahmed Ali*

A. A. M. Ali

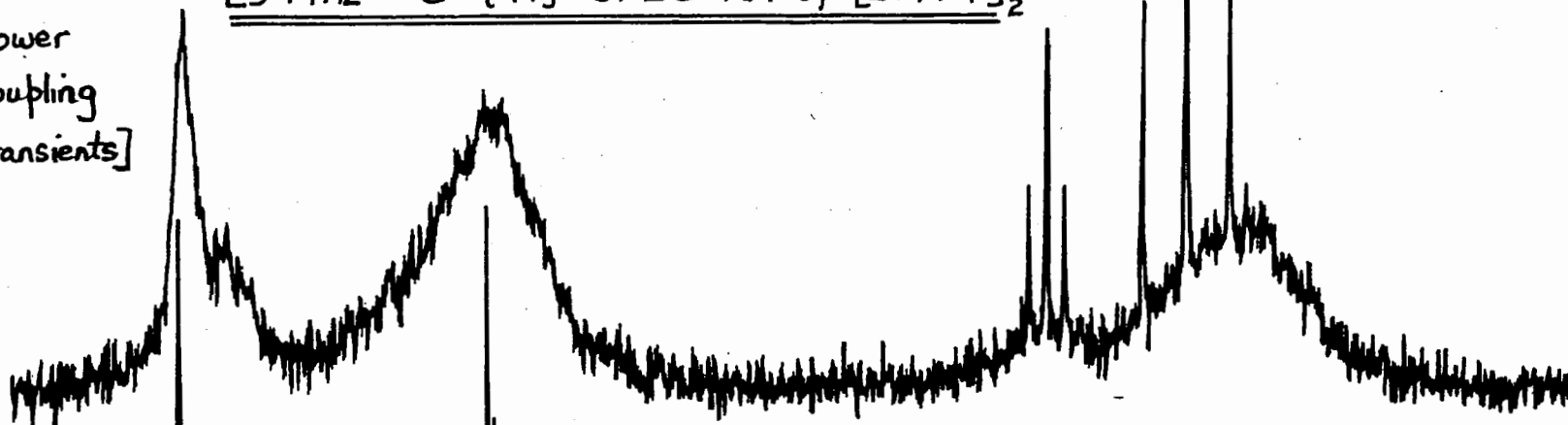
Dr. B. L. Shapiro,  
Department of Chemistry,  
College of Science,  
Texas A & M University,  
College Station,  
Texas 77843,  
U.S.A.

1. S. Aime, R. K. Harris, E. M. McVicker and M. Fild, J.C.S. Dalton, 2144 (1976).
2. idem, J.C.S. Chem. Comm., 426 (1974).
3. R. K. Harris, E. M. McVicker and M. Fild, J.C.S. Chem. Comm., 886 (1975).
4. K. Roth, Org. Magn. Reson. 10, 56 (1977).

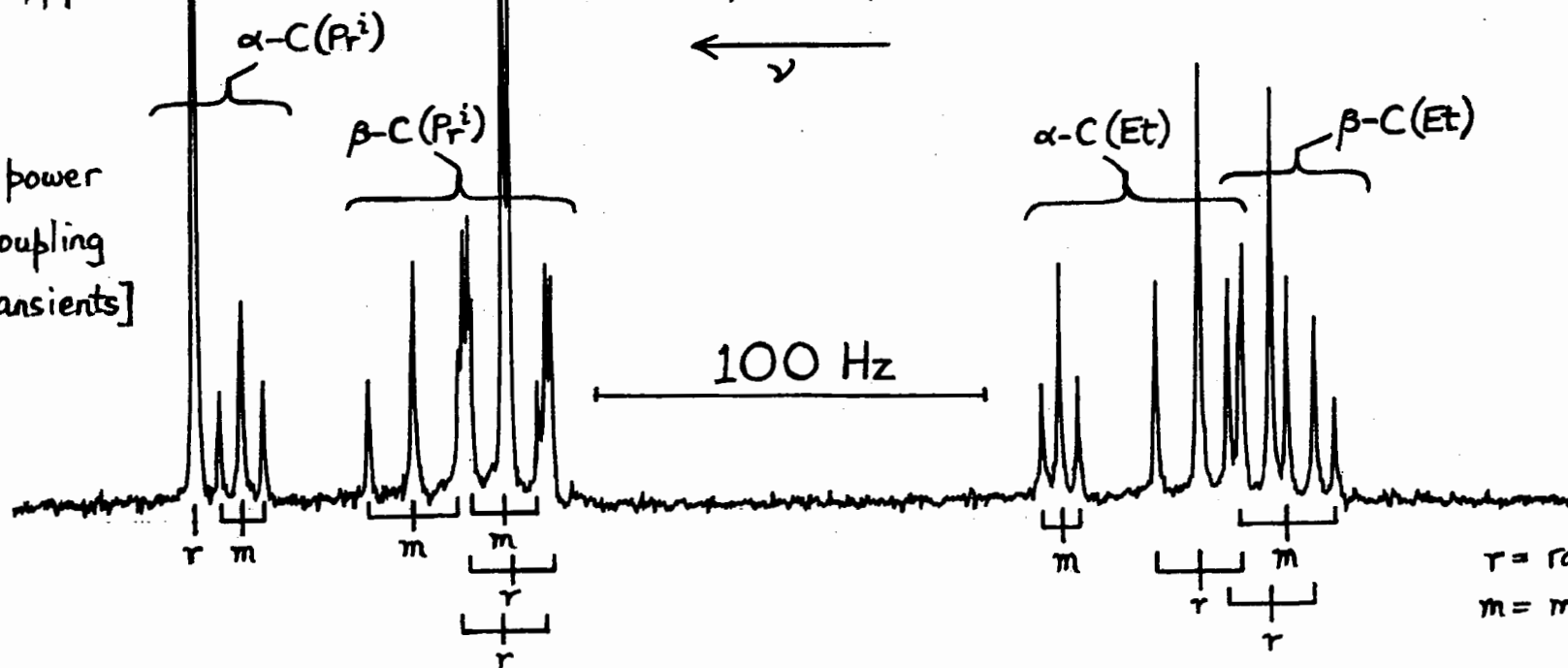
RKH/AAMA/KJS

25 MHz  $^{13}\text{C}-\{^1\text{H}\}$  SPECTRA of  $[\text{EtPr}^i\text{P}]_2$

② Low-power  
 $^1\text{H}$ -decoupling  
[750 transients]



① High-power  
 $^1\text{H}$ -decoupling  
[500 transients]



r = racemic isomer  
m = meso isomer



## TUFTS UNIVERSITY

Department of Chemistry

October 24, 1978

Dr. B. L. Shapiro  
TAMUNMR Newsletter  
College of Science  
Texas A & M University  
College Station, Texas 77843

"Conversational LAOCN3"

Dear Barry:

As an aid to the working spectroscopist as well as the students in my Organic Spectroscopy course, I have rewritten LAOCN3 to operate in a conversational mode from a timesharing computer, in our case, the DECsystem-10. As the program stands, it allows entry of chemical shifts and coupling constants and generates a disk file of transitions and intensities if desired for non-iterating cases. For iterating cases, the transitions can be assigned at the terminal, left blank or duplicate the previous entry. Iteration then proceeds in the usual way. The final values are printed out and if the user has a Tektronix graphics terminal and associated handlers, he can plot the spectrum or any part of it on the terminal. The program will also call the Calcomp plotting routines if desired for hard copy plotting of the result. A typical dialog for an iterated case is attached. The program listing with copious comments or a copy on 9-track magnetic tape is available on request.

We have also developed a simple Huckel MO program which operates in conversational mode which we use in this course as an introduction to the understanding of energy levels used in UV spectroscopy. Both of these programs will be discussed and utilized in a textbook, currently in preparation, on the interpretation of spectra of organic compounds.

Regards,

James W. Cooper  
Assistant Professor

JWC/nmc

Enc.

LAOCOON3

NUMBER OF SPINS= 3

ENTER TITLE: MALIC ACID WITH -J

MIN. FREQ.= 51

MAX FREQ.= 195

ENTER LETTERS FOR EACH NUCLEUS: HHH

V(1)=72

V(2)=83

V(3)=183

J(1,2)= -12

J(1,3)= 7

J(2,3)= 7

ITERATING? (Y OR N): Y

READ IN ASSIGNED TRANS. FROM DISK?(Y OR N): N

MIN. INTENSITY= 0

11	59.672	0.242	56.4
1	66.834	0.284	64.7
15	71.656	1.625	72.0
12	76.119	1.632	79.3
7	78.819	1.849	80.4
2	82.941	1.842	83.7
14	88.103	0.235	94.6
4	94.925	0.291	98.9
8	166.956	0.000	
13	176.240	1.139	176.9
5	183.063	0.993	181.1
9	183.403	0.993	185.1
3	190.225	0.874	189.7

ENTER PARAMETERS TO BE VARIED:

1	1
2	2
3	3
4	12
5	13
6	23
7	0

FINAL VALUES, ITERATION 3

V(1)= 72.103

V(2)= 85.622

V(3)= 182.976

J(1,2)= -15.468

J(1,3)= 9.228

J(2,3)= 3.540

ERRORS IN EACH PARAMETER SET

1	0.078
2	0.077
3	0.049
4	0.070
5	0.093
6	0.097

LAOCOON3

NUMBER OF SPINS= 0

**PURDUE  
UNIVERSITY** BIOCHEMICAL MAGNETIC RESONANCE LABORATORY

October 20, 1978

Barry Shapiro  
Texas A&M University  
College Station, Texas 77843

Title: The Purdue Biological NMR Laboratory is now open for business.

Dear Barry:

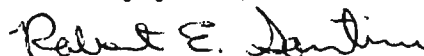
We have set up a high field NMR facility here under the direction of Dr. John Markley. Our present capability is structured around Nicolet NT-360 (8.9T) and NT-150 (3.7T) spectrometer systems. We can operate at  $^1\text{H}$ ,  $^3\text{P}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  frequencies on the 360 MHz system and  $^1\text{H}$ ,  $^3\text{P}$ , and  $^{13}\text{C}$  frequencies on the 150 MHz spectrometer. The NT-150 is a wide bore system and is capable of spinning tubes of 20 mm diameter. We are presently able to provide a large number of custom tailored pulse sequences and experiments to outside users, including correlation spectroscopy and Redfield solvent suppression sequences. It is the mission of this facility to provide regional service for NMR users with biological application in health related fields. Users will be trained to run the system "hands on" or experienced personnel will be available for assistance in collaborative projects. Instrumental development projects will be initiated to further refine the application of NMR to biological problems as the users needs dictate.

Any interested party may obtain further details by contacting our operations manager Dr. Jerry Dallas. At present we are scheduling users' block time on a monthly basis and training sessions are available.

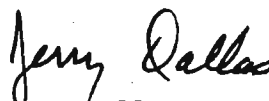
Within the next six months we will upgrade our wide bore system to 200 MHz and our high field system to 450 MHz (or perhaps a higher frequency).

The facility is supported by NIH grant No. RR01077 from the Division of Research Resources. A formal dedication of the facility will have been held on November 17 and 18, 1978. The dedication includes a symposium with outside speakers.

Sincerely yours,



Robert E. Santini  
Director of Instrumentation



Jerry Dallas  
Operations Manager

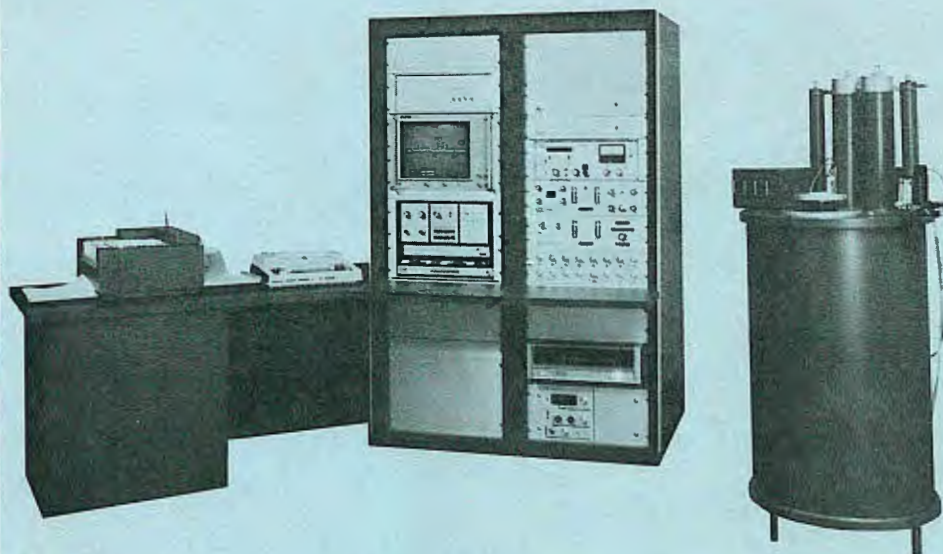


Chemistry Building  
West Lafayette, Indiana 47907  
(317) 749-2438  
(317) 749-2439



# NT-150

## A WIDE-BORE, FT-NMR SYSTEM FROM NICOLET



**For routine NMR and state-of-the-art techniques such as:**

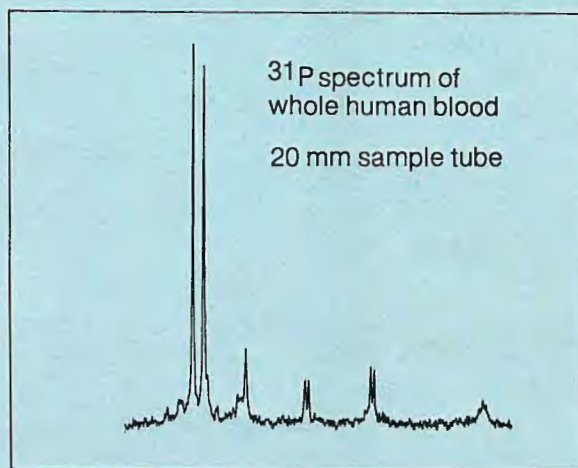
- $^{31}\text{P}$  experiments on living organs.
- Cross-polarization studies on solids.
- $^{13}\text{C}$  studies of high molecular weight polymers.
- Two-dimensional FT-NMR.

### FEATURES INCLUDE:

- 3.5T superconducting magnet with 10 cm room-temperature bore.
- Straight-through access to sample area.
- Quick-disconnect probes for rapid changeover.
- 5, 12 and 20 mm sample tubes as standard, 30 mm optional.
- Quadrature phase detection as standard.
- Computer-controlled audio filter from 100 Hz to 51,100 Hz in 100 Hz steps.
- Nicolet 1180 data system with simultaneous acquisition, processing and plotting.
- Digital plotter with plot lengths selectable from 1 cm to 900 cm.

### OPTIONS INCLUDE:

- NT-150 MF: broad-band multi-nuclei observe for 4 to 60 MHz.
- NT-150 CP: optimized system for Waugh-Pines cross-polarization studies.



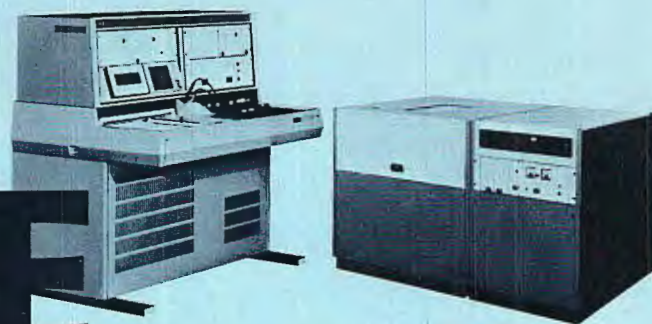
*For more information or to discuss your applications, please telephone or write.*

**NTC** NICOLET  
TECHNOLOGY  
CORPORATION

145 East Dana Street  
Mountain View, California 94041  
Phone: 415/969-2076



# Introducing the **FX90Q** featuring the **OMNI PROBE**



In the continuing development of the FX series, JEOL now offers a compact, 90 MHz, broad-band, FT NMR System at a cost comparable to the lower frequency systems. The "**OMNI PROBE**" is designed to provide the highest performance throughout the **entire** observation range.

#### OMNI PROBE FEATURES:

- **PERMA-BODY**  
Probe head is **fixed** in magnet for continuing optimum performance.
- **PLUG-IN SAMPLE INSERTS**  
10mm V.T. — BroadBand ( $^1\text{N}$  to  $^1\text{H}$ )  
5mm V.T. — BroadBand ( $^1\text{N}$  to  $^1\text{H}$ )  
Micro V.T. / 5mm V.T. / 10mm V.T. — Dual Frequency ( $^{13}\text{C}/^1\text{H}$ )
- **PLUG-IN R.F. MODULES**  
BroadBand ( $^1\text{N}$  to  $^1\text{H}$ )  
Dual Frequency ( $^{13}\text{C}/^1\text{H}$ )
- **IRRADIATION MODULES**  
Proton (standard)
- **LOCK**  
 $^2\text{D}/^7\text{Li}$  Dual Frequency  
internal/external system

#### FX 90Q IS AVAILABLE WITH:

- 90MHz Proton / 22.6 MHz Carbon observation
- Compact **Low Energy** magnet
- Digital Quadrature Detection
- Foreground/Background
- "SHIMPLEX" Auto Y/Curvature controller
- Computer based Multi-Pulse Generation
- $\text{T}_1$ -rho/Spin Locking
- Digital Cassette/floppy disk/moving head disk systems
- Light Pen Control System (LPCS)

# JEOL

235 Birchwood Ave., Cranford, NJ 07016  
201-272-8820