BRIAN SYKES

TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 343

April 1987

Announcing... **AN OUTSTANDING ADDITION TO THE WILMAD NMR LINE...**

our COMPLETELY NEW 5mm "THRIFT" TUBE

at 95¢ each!

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

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

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

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

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

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

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

WILMAD GLASS COMPANY, INC.

Serving the Spectroscopic Aftermarket

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

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

TEXAS A&M UNIVERSITY
NMR
NEWSLETTER

AUTHOR INDEX ------ TAMU NMR NEWSLETTER, NO. 343, APRIL 1987

FORTHCOMING NMR MEETINGS

NMR Data Processing Workshops - May 25, 1987; Zurich, Switzerland; June 2, 1987, Bologna, Italy; and June 18-19, 1987, London, England. For further information, please see p. 33 of this Newsletter.

Blue Hen NMR Symposium - June 1, 1987; University of Delaware, Newark, Delaware. For further information, contact Dr. Lila M. Gierasch, Blue Hen NMR Complex, Chemistry Department, University of Delaware, Newark, Delaware 19716, (302) 451-2739. See page 50 of this issue of the Newsletter for further information.

8th International Meeting "NMR Spectroscopy" - July 5-10, 1987; University of Kent at Canterbury, England; For information, contact Dr. John F. Gibson, Royal Society of Chemistry, Burlington House, London W1V OBN, England. See Newsletter #338, p. 55 for information and application.

29th Rocky Mountain Conference - August 2-6, 1987; Radisson Hotel, Denver, Colorado; Program Chair: Michael Reddy, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002, (303) 236-3617; Nuclear Magnetic Resonance Symposium: James Haw, Department of Chemistry, Texas A&M University, College Station, Texas 77843, (409) 845-1966; Preliminary program and pre-registration information available from Sandy Grande, 8780 W. Quarto Circle, Littleton, Colorado 80213.

In Vivo NMR Spectroscopy Summer School - August 31-September 5, 1987; University of Orleans, Orleans, France. See page 23 of this issue of the Newsletter.

26th Eastern Analytical Symposium - September 13-18, 1987; New York Hilton Hotel, New York, New York; For information, contact J.P. Luongo, AT&T Bell Laboratories, Room 1A-352, Murray Hill, New Jersey 07974, (201) 846-1582.

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.

Fritz Haber International Workshop on Modern Techniques in Magnetic Resonance - December 13-17, 1987; Weizman Institute of Science, Rehovot, Israel; See Newsletter #342, page 7, for additional information.

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 Dr. Charles G. Wade, ENC Secretary, IBM Instruments, Inc., 40 West Brokaw Road, San Jose, California 95110, (408) 282-3641.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence Should be Addressed to:

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

DEADLINE DATES

No. 345 (June) ---------- 29 May 1987

No. 346 (July) ---------- 26 June 1987

USSR Academy of Sciences

Shemyakin Institute
of Bioorganic Chemistry

Ul. Miklukho-Maklaya, 16/10
117871 GSP Moscow V-437
USSR

February 13, 1987
(Received 16 March 1987)

Professor B.L.Shapiro

Department of Chemistry
Texas A & M University
College Station, TX 77843
U S A

Title: Base Plane Correction
in 2D NMR Spectroscopy

Dear Barry,

The base plane distortion in 2D NMR spectra is a headache for at least some of NMR practioners. The problem is especially severe in the phase-sensitive NOESY spectra of biological macromolecules in aqueous solutions if one looks for reliable detection of weak NOE cross-peaks and precise evaluation of cross-peak intesities. To correct the base plane of 2D spectrum $S(\omega_1,\omega_2)$ use was made of an independent polynomial base line correction of rows and columns [1]. An example of base plane correction is shown in Fig. 1. To define a Lagrange polynomial a set of reference points must be selected within each row and each column of 2D spectrum. For that purpose we use reference columns (three reference columns A,B, and C define a set of reference points for all rows of the spectrum) and reference rows (three reference rows A', B', and C' define a set of reference points for all columns of the spectrum), next to which cross-peaks are obviously absent. The polynomial fit of the base lines was made first for rows and then for columns. The effect of the outlined procedure is obvious: (i) t_1 and t_2 ridges as well as strong band caused by the intense H_2O signal are eliminated and (ii) masked cross-peaks are unambiguously revealed. The new peaks are due to intramolecular NOE in agreement with spatial structure of the gramicidin A molecule [2]. The described technique was also successfully aplied in our lab for COSY and other sorts of 2D NMR spectra.

With best wishes

Igor Barsukov Alexander Arseniev Vladimir Bystrov

1. I.L.Barsukov and A.S.Arseniev, J.Magn.Reson. in press (1987)
2. A.S. Arseniev,I.L.Barsukov,V.F.Bystrov,A.L.Lomize and Yu.A.Ovchinnikov, FEBS Letters 186, 168 (1985)

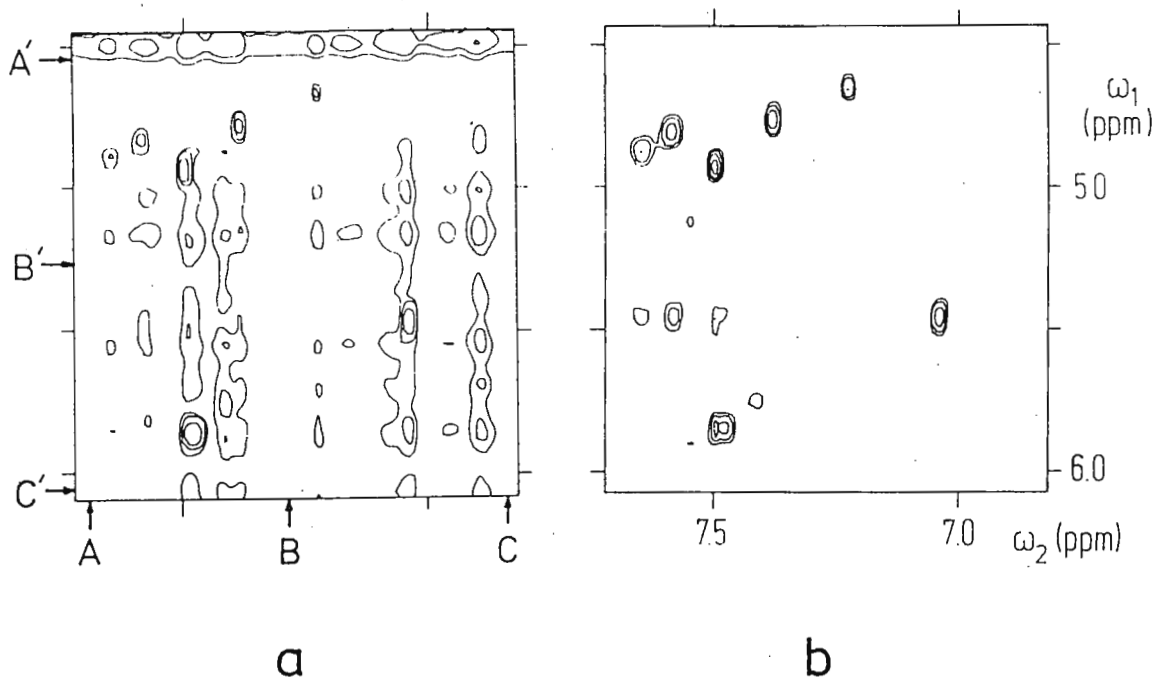


Fig. 1. Contour plots of a region of 500 MHz ^{1}H NMR phase sensitive NOESY spectrum recorded with 5 mM gramicidin A in SDS-d_{25} micelles (peptide/detergent molar ratio 1/50) in H_2O/CF_3CD_2OD (molar ratio 16/1) at 55°C on a Bruker WM-500 spectrometer. Mixing time 100 ms. Digital resolution is 4.8 and 2.4 Hz for ω_1 and ω_2 directions, respectively. (a) Spectrum without base plane correction. (b) The same spectrum after described base plane correction. Identical contour levels are plotted for both spectra.

Koninklijke/Shell-Laboratorium, Amsterdam

Shell Research B.V.

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

(Received 9 March 1987)

Uw ref.: ^{129}Xe NMR vs. Zeolites

Onze ref.: IDC 0376

Amsterdam, 23rd February 1987
Badhuisweg 3
Tel. via telefoniste (020) 30 91 11
Tel. rechtstreeks (020)
Hr/Mw

Dear Professor Shapiro,

We study zeolites from as many angles as we can. The most recent point of view is provided by ^{129}Xe NMR of adsorbed xenon gas. This application has been pioneered by Jacques Fraissard et al. in Paris and by John Ripmeester in Ottawa.

The chemical shift of the xenon resonance has been shown to be a rather sensitive function of the physical environment of the adsorbed atom, decreasing for example as the mean free path increases. In the case described below we may state that in the limit of vanishing xenon concentration the chemical shifts reflect purely the influence of the geometrical restrictions imposed by the zeolite pore space.

The actual NMR is simple. Xenon is a sensitive nucleus and conventional high-resolution conditions can be applied.

One of the zeolites that we have studied by this method is ferrierite. The results obtained prove some of the points above in, we think, a rather appealing way. Ferrierite contains straight pores of dimensions 4.3 x 5.5 Å^2, connected by narrow "windows" to somewhat more spacious cavities. The main feature of the xenon spectra obtained (figs. 1^a - 1^c) is that they consist of two principal peaks, one at constant position irrespective of xenon loading, the other shifting towards lower ppm values as the level of adsorption decreases.

These observations directly reveal details of the zeolite pore structure. The signal independent of xenon concentration is assigned to xenon in the cavities since the latter can hold no more than one Xe atom (no Xe - Xe interactions observed). The variable signal corresponds to xenon in the pores; extrapolated to zero concentration its chemical shift is larger than that of the cavity signal. This tells us that cavities are wider than pores, in agreement with known structural data. (The broad hump beyond 200 ppm is considered of doubtful significance).

Upon closer inspection of the spectra one notices a shoulder upfield of the main peaks. We have shown, by additional MAS work, that this is caused by an anisotropy of the chemical shift.

Koninklijke/Shell-Laboratorium, Amsterdam

An unexpected observation was made when the temperature was reduced. As figs. 2^{a-c} show , xenon appears to be preferentially desorbed from the cavities at low temperature, until at -100 °C the corresponding signal has fully disappeared!

This contribution means a farewell to NMR and all regular TAMU readers for Gary Hays. Since mid-1986 Gary has left NMR to "reinforce" solids and surface analysis (not to forget radiochemistry!) as a supervisor. Colette Alma has taken over his task in NMR and will devotedly continue this TAMU subscription.

Yours sincerely,

KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM

N.C.M. Alma-Zeestraten

G.R. Hays

A.E. Wilson

J.P. van Braam Houckgeest

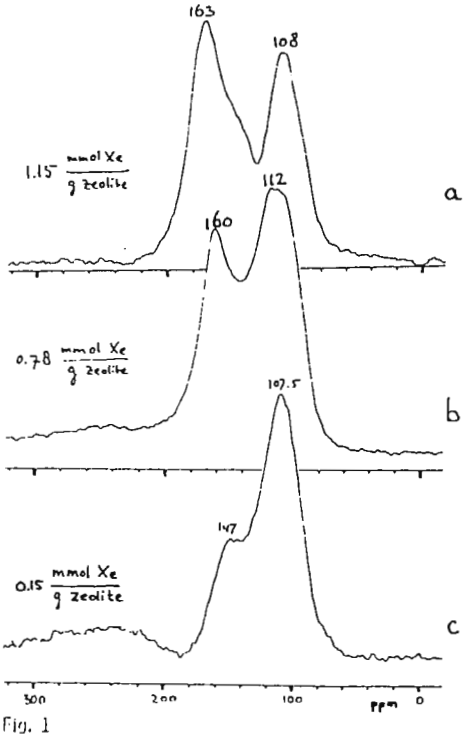


Fig. 1
ROOM-TEMPERATURE SPECTRA OF XENON GAS ADSORBED INTO H-FERRIERITE, AT THREE LEVELS OF ADSORPTION.

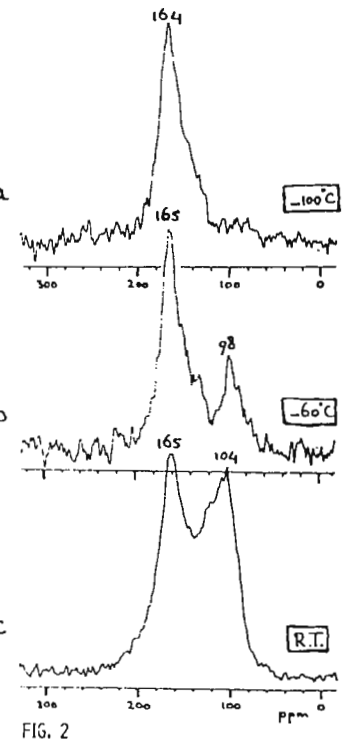


FIG. 2
SPECTRA OF XENON ADSORBED INTO FERRIERITE, AT VARIABLE TEMPERATURE AND CONSTANT XENON LOADING.

Texas A&M University NMR Newsletter - Book Reviews

Book Review Editor - **W. B. Smith,** Texas Christian University, Fort Worth, Texas.

"Carbon-13 NMR Spectroscopy. High-Resolution Methods and Applications in Organic Chemistry and Biochemistry"

by

Eberhard Breitmaier and Wolfgang Voelter

VCH Publishers, Inc., 303 N.W. 12th Ave., Deerfield Beach, Florida 33442
1987; 515 pages; $135.00

This is the third, completely revised, edition of a standard text and reference in the field of ^{13}C NMR spectroscopy. The last edition was in 1978, so the whole world of practical 2D NMR has come upon us since then. This is reflected in the tone of the text, which covers the background material in pulse FT NMR quite completely, and then launches into 2D NMR as applied to ^{13}C specifically. If one were to purchase only one comprehensive volume on this subject, this probably would be the one to acquire.

Following the development of ^{13}C experimental techniques is a discussion of chemical shifts, coupling constants, relaxation times, and dynamic NMR. As read in the English translation, these are well-written, with enough detail and adequate references to be really helpful. The final 284 pages is a survey of chemical shifts selected from compounds of many types, and nicely systematized so one can find one's way to items of interest.

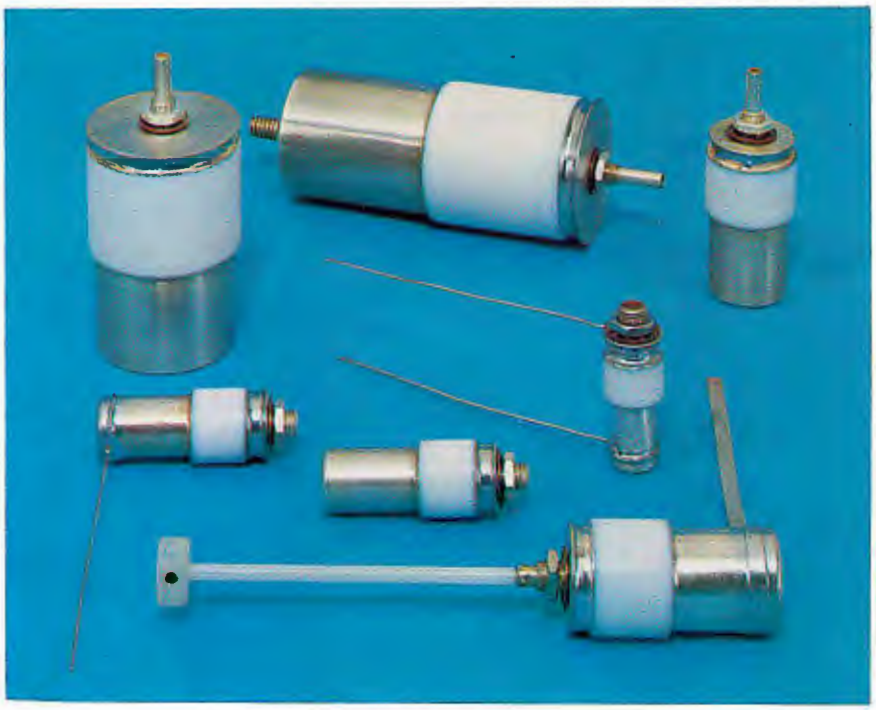
For unstated reasons, the authors have chosen not to cover the ^{13}C NMR spectroscopy of solids. There also is no mention that I can find of WALTZ-16 decoupling, a strange omission. Tragically, the price precludes the use of this book as a classroom text. Practitioners will enjoy having it in the nearest library, if not their own.

W.B.S.

POLYFLON

SERIES VC

High Voltage Non-Magnetic RF TRIMMER CAPACITORS



- ☐ **Non-magnetic**
- ☐ **Q's greater than 5000**
- ☐ **High voltage dielectric**
- ☐ **Test voltages as high as 12 Kv**
- ☐ **Unbreakable Teflon® metal construction**
- ☐ **Operation at frequencies to 1 GHz**
- ☐ **Performance better than quartz, glass or vacuum types**

Polyflon's exclusive Series VC High Voltage RF Trimmer Capacitors provide superior performance, extreme reliability and the highest product durability in a non-magnetic, unbreakable, virtually indestructible package. The reason — Polyflon's unique patented proprietary process of electroplating copper onto Teflon. The resultant mechanical and electrical properties make these trimmers preferred over quartz, glass and vacuum types. Polyflon Series VC Trimmers have operating voltages greater than 6000 volts with extremely low losses ("Q's" exceed 5000). VC Trimmers have successfully been employed at frequencies up to 1 GHz.

The fully non-magnetic properties of the Series VC Trimmers make them ideally suited for Nuclear Magnetic Resonance (NMR) Instruments as probes and tuners. Other applications include Tactical Radios, Radar Transmitter Driver-Amplifiers, High Power Filters, Antenna Tuners, etc. Polyflon Series VC Trimmers are made to meet the most stringent and demanding conditions associated with airborne and shipboard equipment.

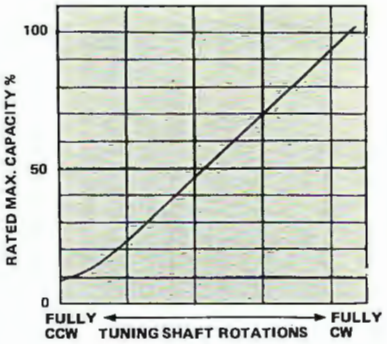
Series VC Trimmers can be provided to meet MIL-Spec requirements. Some units are already available with military part numbers.

Specifications:

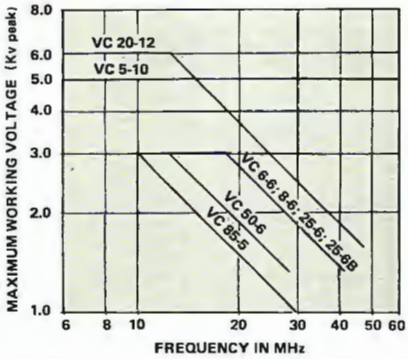
Capacitance Range:	0.7 to 85 pf
Working Voltages:	To 6 Kv
Dielectric Strength:	200% of working voltage, minimum
Quality Factor (Q):	Greater than 5000 to 1 GHz
Insulation Resistance:	10^5 Megohms
Operating Temperature:	−50°C to +150°C*
Temperature Coefficient:	Within 50 ppm/°C
Tuning Torque:	1 to 4 inch ounces

® DuPont de Nemours registered trademark.

POLYFLON SERIES VC



Typical Adjustment Curve VC Series



Voltage/Current Limits (at maximum temperature)

Consult factory for voltage/current ratings under conditions other than cw, at maximum temperature and maximum capacity.

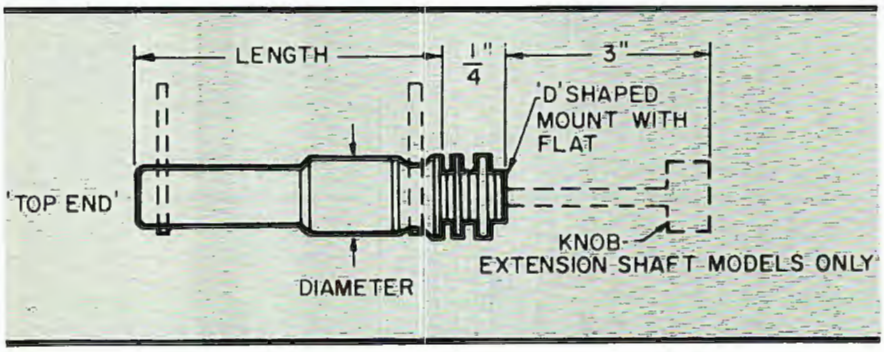
Available as Screwdriver Adjustment or with Extension Shaft. Select Dash No. from Code Table Below.

Model Number	Capacitance Range pf	Peak Working Voltage Kv	Peak Test Voltage Kv	Current (note 1) amps	Nominal Dimensions Inches Length	Inches Dia	Millimeters Length	Millimeters Dia
VC-18-1-(*)	0.7 - 18.	.75	1	1.8	1.13	.43	28.7	10.9
VC-10-12-(*)	0.8 - 10.	6	12	3.3	1.52	0.58	38.6	14.7
VC-5-10-(*)	0.9 - 5.0	5	10	1.65	1.25	0.50	31.8	12.7
VC-6-6-(*)	0.9 - 6.0	3	6	1.25	1.25	0.50	31.8	12.7
VC-8-6-(*)	3.0 - 8.0	3	6	1.7	0.87	0.50	22.1	12.7
VC-25-6-(*)	5.0 - 25.	3	6	5.3	1.43	0.88	36.2	22.4
VC-25-6B-(*)	5.0 - 25.	3	6	4.1	1.48	0.63	37.6	16.
VC-50-6-(*)	5.0 - 50.	3	6	5.3	2.24	1.44	56.9	36.6
VC-85-5-(*)	5.0 - 85.	3	6	5.2	3.25	1.44	82.6	36.6

*Add code number for leads. See Lead Code Number Table below.

Note 1. RMS ampere rating at 16MHz attained by direct connection to capacitor body. Wire leads to straps may limit current to a lower value as a function of application. Most units reactance-limited by working voltage.

Capacitor Outline



Lead Code Number Table

(Unless otherwise specified, units will be supplied as -05 or -06.)

* Code for Screwdriver Adjust Series	Description	* Code for Extension Shaft Series
05	without lead wires	06
15	3" wire, top only—in line with flat	16
25	3" wire, top and bottom—in line with flat	26
35	1½" strap, top only—in line with flat	36
65	3" wire, top only, opposite flat	66
75	3" wire, top and bottom—opposite flat	76
85	1½" strap, top only—opposite flat	86

POLYFLON COMPANY

a Division of UNIDYNAMICS CORP.

35 River St., New Rochelle, N.Y. 10801 (914) 636-7222 TWX: 563 0619

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service

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

March 6, 1987

(Received 12 March 1987)

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

Dear Barry:

We have an opening for an experienced NMR spectroscopist, in the Laboratory of Cellular and Molecular Biology, National Institutes of Health, National Institute on Aging, Gerontology Research Center, in Baltimore, Maryland. This is a Civil Service position and salary depends upon the qualifications of the applicant.

Our laboratory is conducting a number of studies that involve NMR. Molecular studies, such as those on the structure of the active site of RNA polymerase, are being investigated with a Varian XL 200. A Bruker Biospec 1.9T/31 cm is used to study the effect of aging on metabolic changes during human exercise, and the effect of aging on various metabolic phenomena in animals. Other NMR instruments, including 500 MHz, are available in the area, and active collaborations are in progress with Johns Hopkins University. The laboratory is very well equipped with physical chemical, biochemical and biological instrumentation.

The successful applicant will have primary responsibility for NMR operations in the laboratory. He or she will collaborate on the ongoing programs as well as initiate other studies. Technical assistance will be provided.

Please have applicants write to me directly as soon as possible, and include a curriculum vitae and bibliography, and if possible an application for Federal Employment (SF-171). U.S. Citizenship is required. NIH, is, of course, an equal opportunity employer. Further information can be obtained by calling me at 301-955-1805.

Sincerely,

Günther L. Eichhorn
Chief, Laboratory of Cellular
and Molecular Biology

GLE:pab

ETH EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE
ZÜRICH

Laboratorium für anorg. Chemie
PD Dr. P.S. Pregosin
Universitätstrasse 6
Telefon 01 ~~256 41 XX~~ 256 29 15 (28 52)

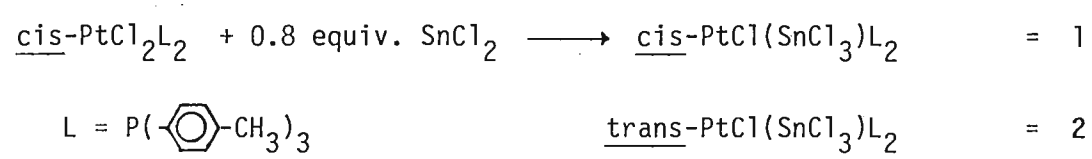
Postadresse:
Laboratorium für anorg. Chemie
ETH-Zentrum
CH-8092 Zürich

March 2, 1987
(Received 16 March 1987)

Prof. Bernard L. SHAPIRO
Texas A&M University
Department of Chemistry
COLLEGE STATION, Texas 77843-3255
USA

Dear Professor Shapiro,

Although 2-D NMR exchange spectra are relatively common for ^{1}H studies, there are relatively few analogs involving ^{31}P. Our long standing interest in the problems of $L_nL_mM\text{-}SnCl_3$ complexes prompted a consideration of the ^{31}P characteristics of the isomers of $PtCl(SnCl_3)(P(p\text{-tolyl})_3)_2$, which arise as shown in the equation.



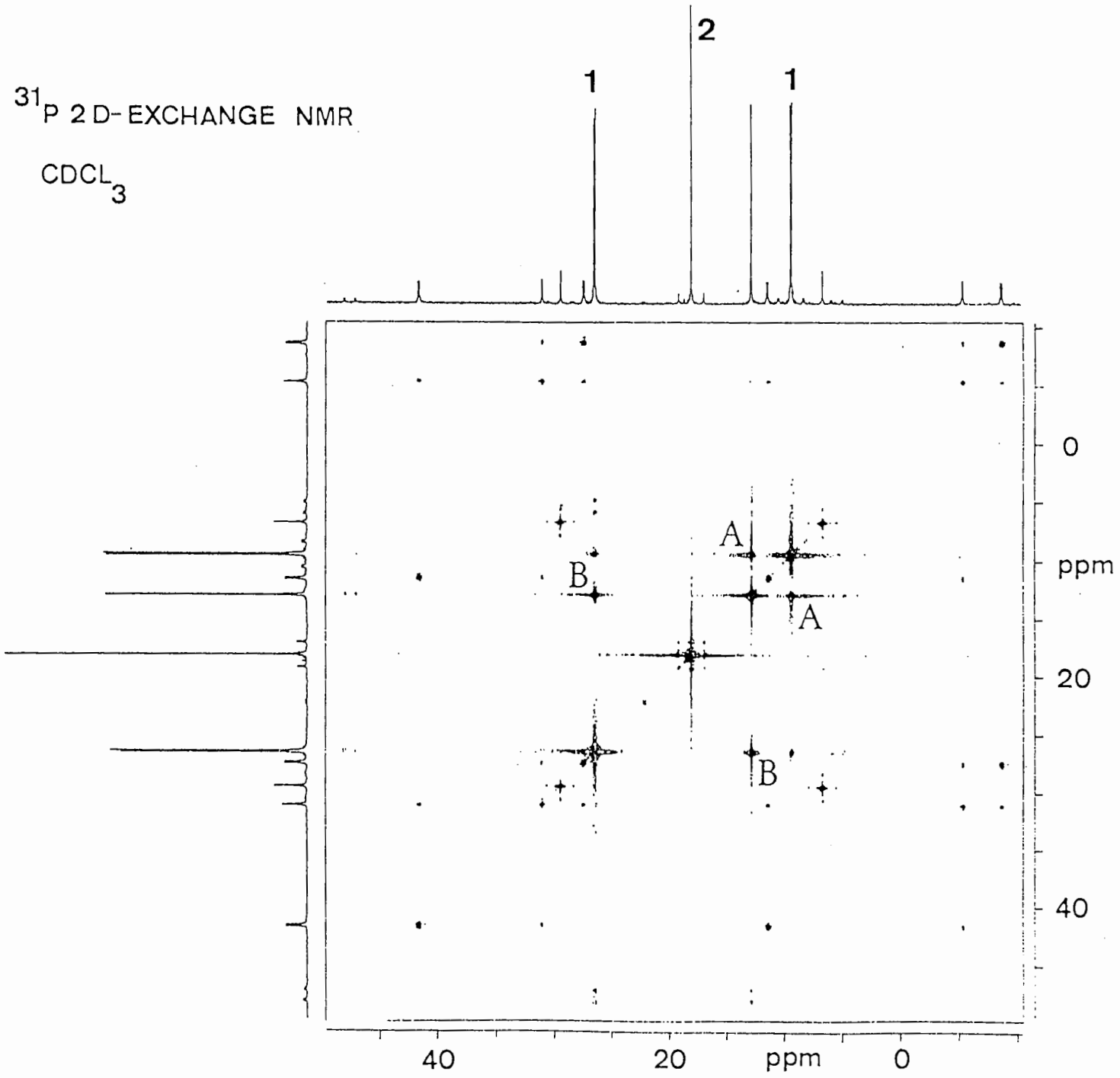
Superficially, the $^{31}P\{^{1}H\}$ spectrum of this mixture of 1, 2 and cis-$PtCl_2L_2$ reveals relatively sharp resonances for all the complexes. Interestingly, the ^{31}P- 2D-exchange spectrum, measured by Heinz Rüegger - Spectrospin AG, Fällanden, reveals that the two ^{31}P environments in 1 a) exchange with the ^{31}P sites in cis-$PtCl_2L_2$ (A,B) and b) with each other. Complex 2 is not involved in these dynamics. Combined with other results we can attribute this relatively slow process to the general reaction: $M\text{-}SnCl_3 \rightleftharpoons M\text{-}Cl + SnCl_2$. A longer exposition of this work is in preparation.

Please credit this contribution to the account of L.M. Venanzi,

Best wishes,

P.S. Pregosin

Suggested Title: ^{31}P 2-D Exchange Studies on Trichlorostannate Complexes of Pt(II).


^{31}P 2D-EXCHANGE NMR
CDCL$_3$
1
2
1
A
B
A
B
0
ppm
20
40
40
20
ppm
0

The University of Alabama at Birmingham
Comprehensive Cancer Center
NMR Core Facility / CHSB B-31
205/934-5696

March 2, 1987
(Received 6 March 1987)

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

Title: Amide Hydrogen Exchange Rates in Complex Carbohydrates

Dear Professor Shapiro,

The exchange rates of amide hydrogens in polysaccharides are of considerable interest because of their proposed role in stabilizing the conformations (by forming intramolecular hydrogen bonds) of complex carbohydrates such as glycosaminoglycans and glycopeptides. Oberholtzer et al. have characterized the conformation of N-linked fetuin glycopeptides by hydrogen-deuterium exchange rate measurements using ultraviolet spectrophotometry and by hydrogen-tritium exchange rate measurements by gel filtration (Biochemistry 20, 4785 (1981)). Our laboratories have been characterizing the group A streptococcal polysaccharide (Fig.1) by high-field NMR spectroscopy. Since the exchange life times of the amide hydrogens in this polysaccharide are relatively short (and comparable to the spin-lattice relaxation times), we have employed a nuclear magnetic double resonance technique involving a combination of two separate experiments: (i) the transfer of solvent saturation and (ii) the amide hydrogen saturation recovery NMR experiments, to measure the amide hydrogen exchange rates in H_2O. All the measurements were performed on the carbohydrates dissolved in H_2O (with 10% D_2O for lock) using either the 2-1-4 or the 1-3-3-1 pulse sequences. This double resonance technique has been previously employed in the conformational studies of many biologically active peptides.

The amide hydrogen exchange rates (at 25°C) for the polysaccharide are shown in Fig 2 (open circles). A small systematic error (which was anticipated) in the exchange rates due to nonspecific spin diffusion in the polymer was easily estimated and the data were corrected. This error, however, is negligible above pH 6 where the solvent exchange rates predominate. Also shown in Fig. 2 are the exchange rates for a solvated model compound, 1-O-methyl-2- acetamido-2-deoxy-β-D-glucopyranoside (filled circles). The solid line is a least squares fit through the model compound data, and corresponds to a base catalyzed rate constant of $k_{OH}=2.64 \times 10^7\ M^{-1}s^{-1}$ at 25°C.

Since the amide hydrogen exchange rates for the group A streptococcal polysaccharide show excellent agreement with the model compound data, we conclude that the acetamido hydrogen in this polysaccharide exists essentially in a solvated environment, and that it does not contribute to the conformational stability of the polymer by intramolecular hydrogen bonding. Thus the biological function, if any, of the lone acetamido hydrogen remains intriguing. Experiments are currently underway to extend these studies to other complex carbohydrates that contain several chemically distinct amide hydrogens.

Yours sincerely,

D.H. Huang D.G. Pritchard T.T. Sakai N.R. Krishna

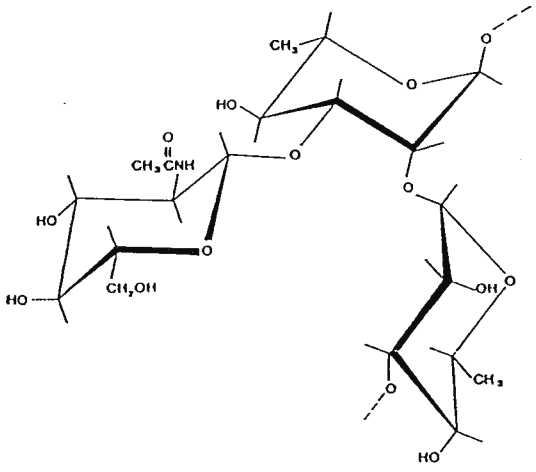


Figure 1:
Repeating unit of group A streptococcal polysaccharide

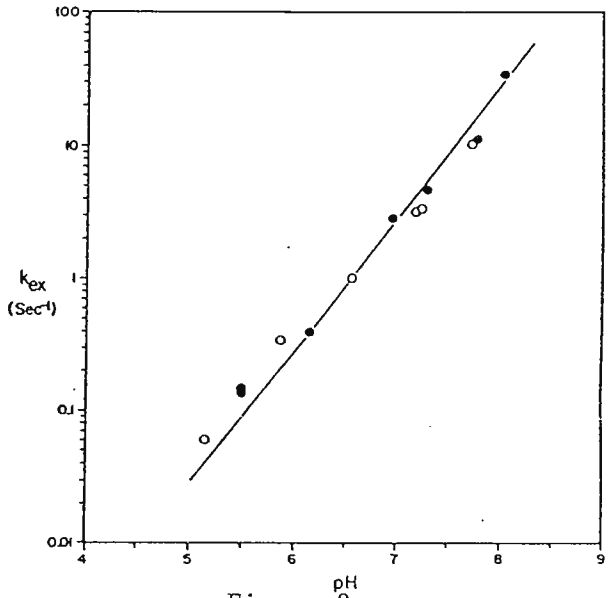


Figure 2:
Comparison of the acetamido hydrogen exchange rates for the polysaccharide and the model compound

CSIR

Council for Scientific and Industrial Research

National Chemical Research Laboratory

P O BOX 395 PRETORIA 0001 SOUTH AFRICA

Telephone: National (012) 86-9211
International + 27 12 86-9211

Teletex: 350180 = CSIR
Telegrams: Navorschem

Telefacsimile: National (012) 86-2856
International + 27 12 86-2856

Our file: 600/300/87/1 Your file:

Professor Bernard L Shapiro
Department of Chemistry
Texas A & M University
COLLEGE STATION
TEXAS 77843
United States of America

26 FEB 1987

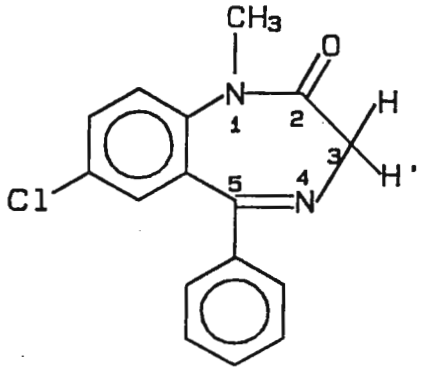
(Received 6 March 1987)

Dear Professor Shapiro

$^{13}C\{^{1}H\}$ SPI AND SELECTIVE $\{^{1}H\}$ DECOUPLING

The assignment, magnitude and sign of two and three bond (C,H) coupling constants are important for numerous nmr studies. It is sometimes difficult to extract these values from the coupled ^{13}C nmr spectrum. This is especially the case where the carbon atom couples to a number of protons, which frequently happens.

In diazepam (I) the geminal and vicinal (C,H) coupling constants from the individual C-3 methylene proton to C-2 and C-5 are expected to be different. The additional couplings of the methyl protons to C-2 and aromatic protons to C-5 make it, however, difficult to determine any geminal or vicinal (C,H) coupling constants from these carbon atom resonances as is obvious from the coupled ^{13}C nmr spectrum reproduced in Figure 1a.



(I)

The methyl protons or the aromatic protons can be selectively decoupled, leaving only the couplings from the C-3 methylene protons to C-2 and C-5. Figure 1b shows the resonances of C-2 and C-5 with the aromatic protons selectively irradiated. Proton decoupling, because of the off-resonance effect, normally reduces the magnitude of the remaining (C,H) couplings.

The individual (C,H) coupling constants have been assigned and the signs determined from SPI experiments [1] and selective proton decoupling during acquisition (see Figures 1c and d). Accurate values for the (C,H) coupling constants were obtained from SPI experiments without selective proton decoupling (shown in Figure 1e) and the coupled ^{13}C nmr spectrum (see Figure 1a). The relevant nmr results are given in Table 1.

Table 1 Relevant nmr data of diazepam (I)

	δ (ppm)	J (Hz)		
		H	H'	Others
C-2 C-5	169.46 168.50	-5.87 +11.26	-5.87 +7.19	3.17 (CH_3) 4.06 (aromatic protons)
3-H 3-H'	4.774 3.726			-10.76 ($^2J(H,H')$)

Yours sincerely

P L WESSELS
HEAD: STRUCTURAL CHEMISTRY

1. A.A. Chalmers, K.G.R. Pachler and P.L. Wessels, Org. Magn. Reson., 6, 445 (1974).

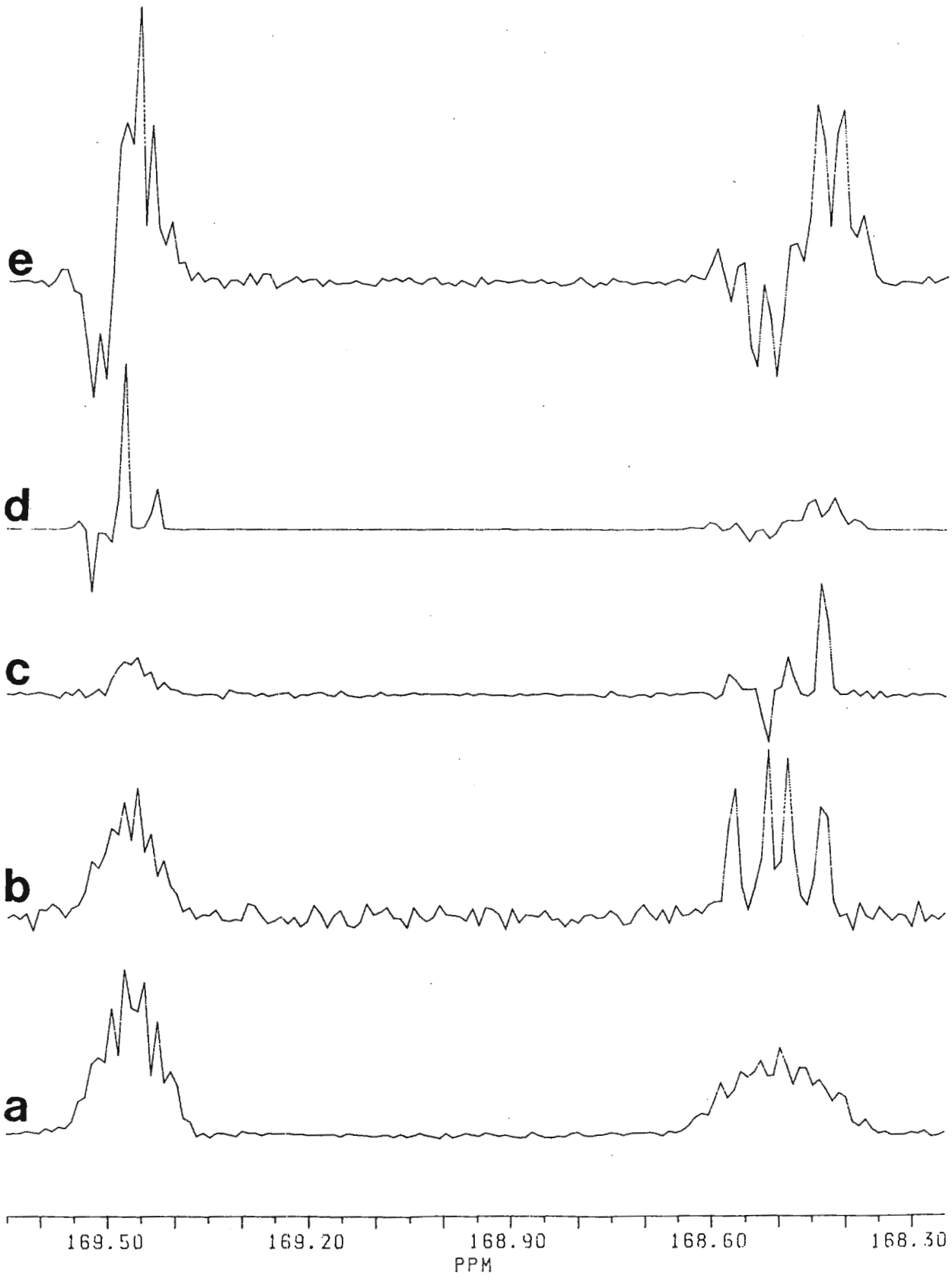
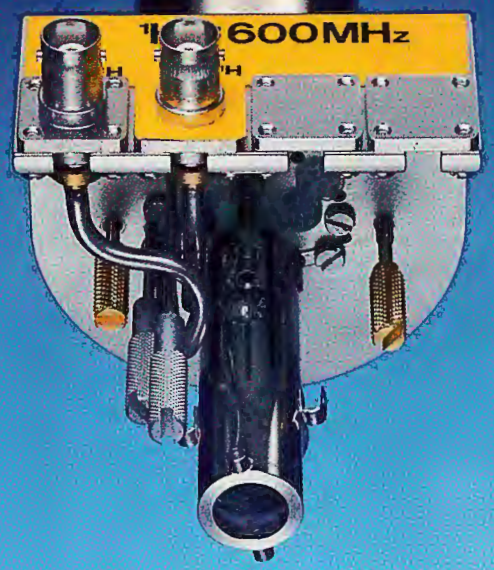


Figure 1 ^{13}C nmr spectra of C-2 and C-5 of diazepam (I). (a) Coupled. (b,c,d) Aromatic protons selectively decoupled. (c) Selective π-pulse (γH_2 = 5 Hz) applied to highest frequency transition of 3-H. (d) Selective π-pulse applied to lowest frequency transition of 3-H'. (e) Only a selective π-pulse applied to highest frequency transition of 3-H.

Bruker delivers.



Again.

Since its foundation in 1960, Bruker has continued to make major contributions to the field of commercial analytical instrumentation, especially NMR:

1963: World's first pulsed NMR spectrometer.

1967: World's first truly multinuclear high resolution NMR spectrometer.

1969: Introduction of Fourier transform techniques for NMR.

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

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

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

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

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

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

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

BRUKER *NMR Systems designed to solve problems.*

Support and Services

Applications Support: Our worldwide application laboratories have earned a reputation for being responsive to your specific requests. It is this commitment to support which is your prime benefit.

Service: We know how vital instrument availability is. That's why we continue to place our factory-trained service engineers in strategic locations as close to you as possible. We offer maintenance contracts in addition to our basic full year warranty.

Technology Support: We actively support the exchange of ideas within the NMR community through sponsorship of many international and local meetings and associations, and through participation in major symposia and exhibitions. Our newsletter BRUKER REPORT keeps you informed about technical developments and new applications. If you have any questions about NMR, let us know. We are totally committed to you and to NMR.

Sales and Service Offices in the USA:

BRUKER INSTRUMENTS, INC.
Manning Park
Billerica, MA 01821
(617) 667-9580
Telex: 200254+947125
Fax: 617-667-3954

Sales/Analytical Instruments:
(617) 667-4614

Sales/Medical Instruments:
(617) 663-7406

Service:
(617) 667-9585

California
BRUKER INSTRUMENTS, INC.
2880 Zanker Road
Suite 106
San Jose, CA 95134
(408) 434-1190

Chicago
BRUKER INSTRUMENTS, INC.
5111 Academy Drive
Lisle, IL 60532
(312) 971-4300

Delaware
BRUKER INSTRUMENTS, INC.
3411 Silverside Road
Webster Building
Suite 107, Concord Plaza
Wilmington, DE 19810
(302) 478-8110

Houston
BRUKER INSTRUMENTS, INC.
9450 Grogans Mill Road
Suite 115
The Woodlands, TX 77380
(713) 292-2447

Bruker Worldwide:

W.-Germany:
BRUKER ANALYTISCHE
MESSTECHNIK GMBH
Silberstreifen, D-7512 Rheinstetten 4
Tel. (07 21) 51 61-0, Tx. 7 826 836

BRUKER ANALYTISCHE
MESSTECHNIK GMBH
Wikingerstrasse 13
D-7500 Karlsruhe 21
Tel. (07 21) 59 67-0, Tx. 7 825 656

BRUKER-FRANZEN
ANALYTIK GMBH
Kattenturmer Heerstrasse 122
D-2800 Bremen 61
Tel. (04 21) 87 00 80, Tx. 2 46 404

Switzerland:
SPECTROSPIN AG
Industriestrasse 26
CH-8117 Fällanden
Tel. (01) 825 48 55-59, Tx. 54 850

Australia:
BRUKER (Australia) Pty. Ltd.
P.O. Box 21, Earlwood
New South Wales, Australia 2206
Tel. 02-5589747, Tx. 70880

Belgium:
BRUKER SPECTROSPIN S.A./N.V.
Rue du Vindictive-Straat 2
B-1040 Bruxelles
Tel. (02) 7 36 11 38, Tx. 25.797

Canada:
BRUKER SPECTROSPIN LTD.
555 Steeles Avenue, East Milton
Ontario L9T 1Y6
Tel. (416) 876-4641, Tx. 06-961446

England:
BRUKER SPECTROSPIN LTD.
Unit 3, 209 Torrington Avenue
GB Coventry CV4 9HN
Tel. (0203) 46 37 70, Tx. 31 649

England:
OXFORD RESEARCH SYSTEMS
LIMITED
Nuffield Way, Abingdon
Oxon OX 14 1RY
Tel. (02 35) 3 24 21, Tx. 83 356

France:
BRUKER SPECTROSPIN SA
34, rue de l'Industrie
F-67160 Wissembourg
Tel. (088) 94 98 77, Tx. 870639

India:
BRUKER INDIA
SCIENTIFIC Pvt. Ltd.
c/o Materials Research Instruments
63, (B-Wing) Mittal Court
Nariman Point, BOMBAY–400 021
Tel. 23 20 44, 23 02 98, Tx. 116096

BRUKER INDIA SCIENTIFIC
522, Raj Mahal Vilas Extn.
11th A cross, Sadashivnagar
BANGALORE–560 080
Tel. 36 25 20

Italy:
BRUKER SPECTROSPIN SRL
Via Giovanni Pascoli, 70/3
I-20133 Milano
Tel. (02) 23 50 09, 2 36 40 69
Tx. 331 263

Japan:
BRUKER JAPAN CO. LTD.
21-5, Ninomiya 3-chome
Yatabe-Machi, Tsukuba-Gun
IBARAKI 305
Tel. 0298-52-1234, Tx. 3652571

Netherlands:
BRUKER SPECTROSPIN NV
Bruynvisweg 18
NL-1530 AB Wormer
Tel. (75) 28 52 51, Tx. 19 197

Scandinavia:
BRUKER SPECTROSPIN AB
Sågvägen 12
S-18400 Åkersberga
Sweden
Tel. (07 64) 6 80 60, Tx. 15 725

Department of Molecular Physics

Wageningen Agricultural University

Your reference
Your letter of
Our reference
Enclosure(s)
Date

March 6, 1987
87/152 KPD:jwb

March 19, 1987

(Received 27 March 1987)

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

Re HIGH POWER ^{1}H-DECOUPLED ^{2}H NMR OF LIPOSOMES

Dear Professor Shapiro,

Recently we have started the investigation of the interaction of viruses with model membranes [1,2]. The objective of the research is to study the initial steps of the infection mechanism of non-enveloped viruses at a molecular level. This work, which was presented recently in Todtmoos (Germany) [3], is an extension of our previous NMR work on the assembly and disassembly of viral particles [4].

In the course of our work on bacteriophage M13 coat protein, using selectively deuterated palmitic acid as a bilayer probe [2], it was found that the presence of 9 w% M13 coat protein did not affect the quadrupolar splitting in liquid-crystalline phase lipids. However, the protein increased the linewidth in the spectra of the palmitic acid (27 w% in DMPC liposomes), labeled at the C-9 and terminal C-16 position (Fig.1).

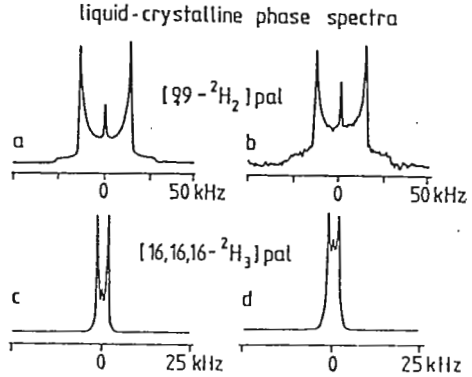


Figure 1. 46 MHz ^{2}H NMR spectra of C-9 (a,b) and C-16 (c,d) labeled palmitic acid (27 w% in DMPC liposomes) in absence (a,c) and in presence (b,d) of 9 w% M13 coat protein.

■ postal address P.O.B. 8091 / 6700 EP Wageningen / The Netherlands
office Transitorium / De Dreijen 11 / Wageningen / The Netherlands
telephone + 31 83 70 8 20 44 if no reply + 31 83 70 8 26 34
telex NL 45015

This effect of the coat protein on the ^2H NMR linewidth is best studied by direct measurement of T_{2e}. In addition, we employed high power ^1H-decoupled ^2H NMR to separate the contribution of the dominant relaxation mechanisms for selectively deuterated acyl chains in liposomes, i.e. (1) quadrupolar relaxation due to the electric field gradient, and (2) dipole-dipole relaxation due to couplings with protons, that can be intramolecular and intermolecular.

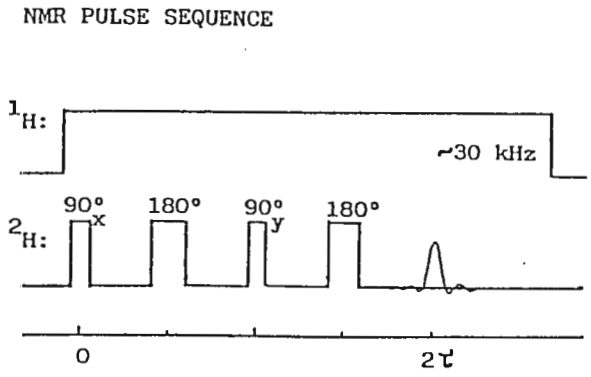


Figure 2. Pulse sequence for high power ^1H-decoupled ^2H NMR measurements. Typical conditions: 90° puls length 3 μs, relaxation delay 333 ms and $\nu 1_H$ = 30 kHz.

In Fig.2 the pulse sequence is shown. The 180° pulses are inserted to also refocus possible dephasing effects from dipolar interactions. The results are given in Table 1.

Table 1. Calculated contributions to the ^2H NMR linewidth (Hz) of the quadrupolar (Δ_q) and dipolar (Δ_d) relaxation.

label	gel (0°C)		liquid-crystalline (45°C)	
	Δ_q	Δ_d	Δ_q	Δ_d
C- 9	910	680	590	60
C-16	250	250	60	<10

From these measurements we conclude that:

(1) In the gel phase the dipolar and quadrupolar contributions to the spectral linewidth are of equal size. Contrary to perdeuterated acyl chains, the dipolar relaxation should be taken into account if selectively deuterated bilayer probes are used;

(2) In the liquid-crystalline phase the dipolar contributions are small and negligible. Possibly the intermolecular dipolar relaxation is small due to the fast lateral diffusion of the lipid molecules and a reduced molecular packing.

We plan to continue these experiments for the investigation of the incorporation of viral proteins in lipid systems.

Sincerely,

Klaas P. Datema P. Adrie de Jager Marcus A. Hemminga

References

1. M.A. Hemminga (1987). J. Chem. Soc. Faraday Trans. 1 83, 203-210.
2. K.P. Datema, R.B. Spruijt, C.J.A.M. Wolfs and M.A. Hemminga (1987), submitted for publication.
3. K.P. Datema, P.A. de Jager and M.A. Hemminga (1986). Abstr. 12th Int. Conf. on Magn. Reson. in Biol. Syst., p. 123.
4. M.A. Hemminga, K.P. Datema, P.W.B. ten Kortenaar, J. Krüse, G. Vriend, B.J.M. Verduin and P. Koole (1985), in Magnetic Resonance in Biology and Medicine (G. Govil, C.L. Khetrapal and A. Saran, Eds.), pp. 53-76. Tata McGraw-Hill, New Delhi, India.

P.S. Please credit this contribution to dr. Schaafma's account.

UNIVERSITY OF CALIFORNIA, DAVIS

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

UCD NMR FACILITY

DAVIS, CALIFORNIA 95616

March 2, 1987
(Received 9 March 1987)

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

CARBON-PROTON SHIFT CORRELATION IN A PARAMAGNETIC SYSTEM

Dear Professor Shapiro:

Recently we have been interested in making proton assignments in hemoprotein spectra via use of reconstituted C13 enriched hemins. The traditional method we had employed in the past to locate the bonded protons would be a series of careful single frequency decouplings while observing C13. In the case of closely spaced proton signals this method can give ambiguous results.

It seemed advantageous to apply a more modern approach to the problem, namely the 2D carbon-proton shift correlation experiment (hetero COSY). It was our initial belief that the main barrier to successful performance of the experiment would be the rapid paramagnetic relaxation of heme systems. The pulse sequence we used was the basic one descibed by Bax (1). Ignoring for simplicity decoupling considerations, the pulse sequence is 90-t_1-90 on the protons followed by a carbon 90 pulse. The difficulty one encounters in paramagnetic complexes is that as t_1 increases proton T2 relaxation will rapidly diminish the coherence needed to effect magnetization transfer between the coupled C13 and 1H spins, reducing or even eliminating cross peaks arising from coupled nuclei.

However, we have found that it is possible to obtain hetero COSY spectra in heme complexes provided that the proton T_2 is sufficiently long and that one recognizes that the maximum t_1 is restricted. Presented in Figure 1 is a hetero COSY spectrum correlating the carbon and proton signals of a sample of bis-cyano ligated hemin with both alpha-propionate carbons 90% enriched in C13. The spectrum was acquired on an NT-360 with carbon observation. The maximum t_1 value was 11 msec.

The successful extension of this method to hemoproteins and its limitations will be more fully discussed in a forthcoming paper.

Sincerely,

Jeffrey S. de Ropp Jacqueline L. McGourty Gerd N. La Mar

Jeff Jackie Gerd

1) A. Bax, "Two-Dimensional Nuclear Magnetic Resonance in Liquids", D. Reidel Pub. Co. 1982, Chapter 2.

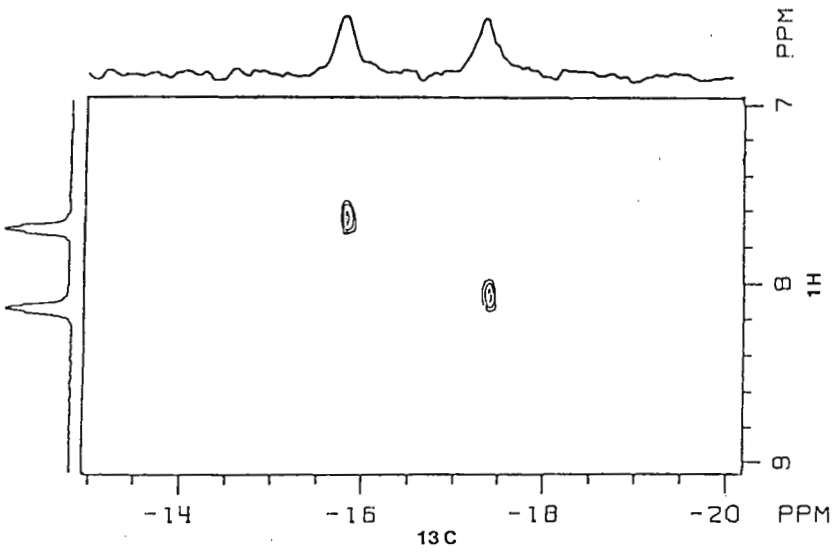


Figure 1: Carbon-proton heteronuclear correlation spectrum, heteronuclear decoupled in each dimension, obtained with C13 observation at 90.5 MHz.

INSTITUT DE RECHERCHE FONDAMENTALE

DÉPARTEMENT DE RECHERCHE FONDAMENTALE DE GRENOBLE

SERVICE DE PHYSIQUE

Groupe Résonance Magnétique
en Biologie et Médecine

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

N/Référence: DRF/SPH/RMBM/87-11/NF

Grenoble, le 19 Mars 1987

Dear Dr Shapiro,

In vivo NMR spectroscopy is the subject of a summer school at the University of ORLEANS (France) scheduled for August 31 - September 5, 1987. French will be the main langage of the meeting. Further information can be obtained from Professor J.P. GRIVET, Centre de Biophysique Moléculaire, C.N.R.S, 1 Avenue de la Recherche Scientifique 45071 ORLEANS Cedex 2, France.

We would highly appreciate it if you had published this information in your TAMU NMR Newsletter.

Sincerely yours

A. DECORPS

Centre d'Etudes Nucléaires de Grenoble, DRF/SPh
85 X, 38041 Grenoble Cedex, France

Téléphone: 76 88 44 00
Télex: ENERGAT GRENO N° 320-323

UNIVERSITÄT TÜBINGEN
PHYSIKALISCHES INSTITUT
Prof. Dr. O. Lutz

D-7400 TÜBINGEN 1, den 04.03.1987
Morgenstelle
Telefon (0 70 71) 29 67 14

(Received 9 March 1987)

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

^{11}B NMR in dilute aqueous solutions

Dear Barry,

in the last time we have performed ^{11}B NMR measurements in aqueous solutions at very low concentrations since there is some interest in investigations on the element boron in waste and tap water and biological fluids. Solutions of boric acid, borates, tetraborates, and pentaborates have been investigated down to 1 millimolal solutions. The pH of the different salt solutions plays an important role since the equilibrium between $B(OH)_3$ and $B(OH)_4^-$ defines the linewidths and chemical shifts observed. For borate solutions with concentrations lower than 20 millimolal an unexpected behaviour has been found: the line widths increase and chemical shifts are observable. In the figure a time dependence is presented, the origin of this effect is not clear at the moment. Further results are given in:

Z. Naturforsch. 41a, 737(1986),
R. Balz, U. Brändle, E. Kammerer, D. Köhnlein, O. Lutz,
A. Nolle, R. Schafitel, and E. Veil,
^{11}B and ^{10}B NMR Investigations in Aqueous Solutions.

Sincerely

(Otto Lutz)

^{11}B in solutions of $NaBO_2$ in H_2O

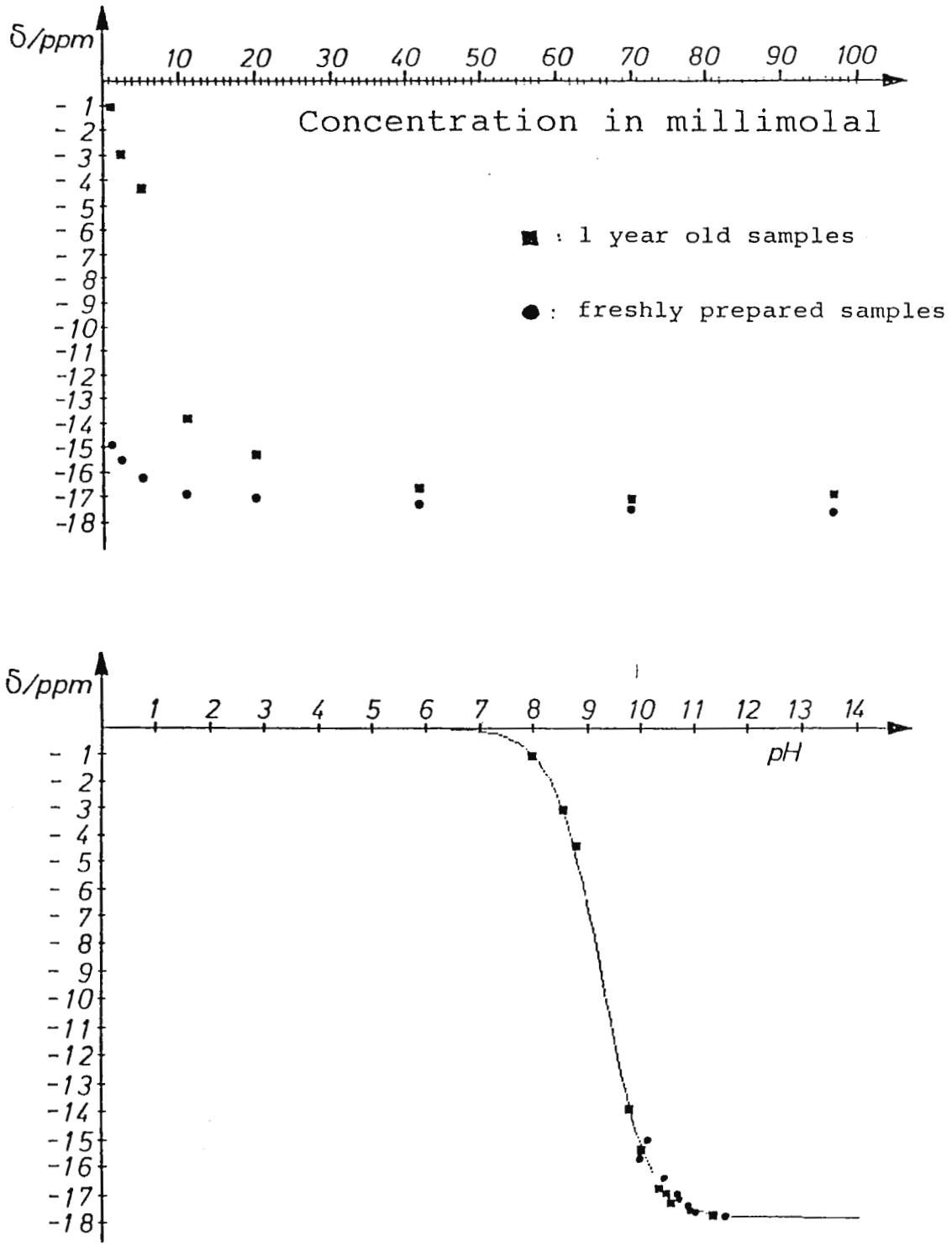


Fig: ^{11}B chemical shifts ($B(OH)_3$: 0 ppm) as a function of concentration and pH for $NaBO_2$ in H_2O. The curve given in the lower part is calculated with pK_s = 9.2.

UNIVERSITE DES SCIENCES ET TECHNIQUES DU LANGUEDOC

GROUPE DE DYNAMIQUE DES PHASES CONDENSEES
Laboratoire Associé au C.N.R.S. N° 233

Montpellier, March 5 , 1987
(Received 18 March 1987)

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

Simulation of the NMR signals given by a Magnetic Resonance Imaging system

Dear Professor Shapiro,

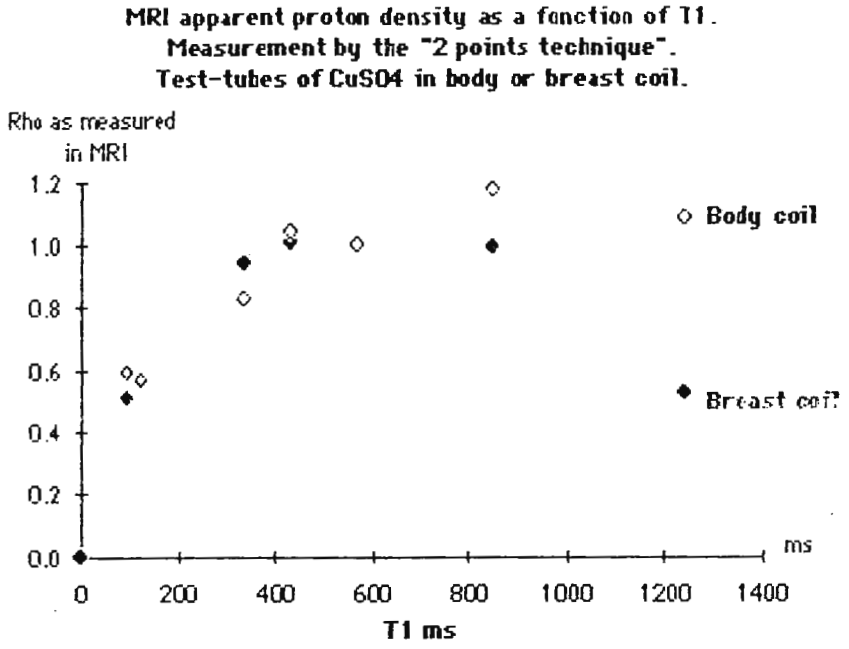
It may be very usefull, when using Magnetic Resonance Imaging (MRI), to be able to simulate signal and contrast evolution for healthy or pathological tissues. This is very easy to do in theory with a microcomputer, when one knows the relaxationnal paramaters (ρ,T_1,T_2) for the tissues and exact equations, or good approximations, for the NMR sequences to be used. This technique has been described by many authors, essentially to explain images obtained by MRI from the nervous system, mainly the brain [1,2], but when one wants to apply this simple approach to obtain directly quantitative data, some difficulties may appear, depending on the imager used and on how it transforms and reproduces NMR signals.

We analysed this NMR signal restitution in our imager (Magniscan 0.35 T from C.G.R.) by mean of test-tubes filled with paramagnetic solutions of known ρ, T_1 and T_2.

Images where generated using Spin-Echo or Inversion-Recovery sequences, and ρ was evaluated by mean of an adapted program or by analysing apparent contrast between different test-tubes.

We observed an "apparent proton density" whose value depended on T_1 and on the antenna used (see figure). This aspect could be interpreted as a signal saturation inside the image for low T_1 values, and by magnetic saturation and tip angle inexactitude for long T_1 in certain surface coils (breast, for instance).

As already mentionned by some authors [1,3], efficient simulation of NMR signals and contrasts must take real values of ρ into account. This shows the great importance of the apparent T_1 dependance of ρ in an imager - if it does exist -, and the necessity of studying such a phenomenon in that particular imager on which one works



Nota: Rho app. = 1 for T1 = 570 ms

This dependance is for us one of the conditions to obtain good simulations of the NMR signal evolution as seen in our MR Imaging system, but we have to take into account some other important aspects as the apparently multiexponential evolution of T_1 as measured by an appropriated method in MRI.

Sincerely,

Michel Zanca,
PhD, MD, Biophysicist

Patrick Bernier
PhD, NMR Physicist

[1] - WEHRLY F.W., Mac FALL J.R , NEWTON T H., in "Modern Neuroradiology" (1983), Newt and Potts D.G. Edts, Clavadel Press Publisher
[2] - WEHRLY F.W. et al., Investigative Radiology, **20**,(1985), 360-369
[3] - DESGREZ A., BITTOUN J., J. Biophysique Médecine Nucléaire,**8(2)**,(1984),41-43

BERLEX Laboratories, Inc.
Subsidiary of Schering AG, West Germany

Department of Medicinal Chemistry

March 3, 1987
(Received 9 March 1987)

ULTRACHEAP NMR IMAGING — USE OF AN UNMODIFIED XL-300 TO PERFORM LAUTERBUR'S EXPERIMENT

Dear Barry:

One day when things were a little slow in the lab, I began to wonder if the shim coils on my XL-300 might provide enough of a gradient to do some rudimentary imaging. To check this out I took a couple of melting point capillaries (KIMAX-51, 1.5-1.8mm x 90mm), filled them with water, placed them in a 5mm NMR tube which I then inserted into my XL-300 magnet equipped with the 5mm $^{1}H/^{19}F$ probe. Next I cranked my X-axis shim coil setting away from its usual value of 500 up to a new setting of 600 and, lo and behold, the nice, sharp single line that I saw at 500 (Figure Ia) separated into two broadened lines at 600 (Figure Ib). Rotating the tube around a few times (by turning the spinner on and off) I found that the maximum separation that I ever observed was about 45 Hz. My best estimate of the separation of the center of the tubes is 2.7mm. This would suggest the presence of a gradient at this setting of 17 Hz/mm (about 0.4 mT/m for this field, or roughly 1/10 that typically used in commercial clinical imagers. This gradient is about 1/4 that employed by Lauterbur[1]). Taking into account the increased linewidth, I estimate that the smallest separation that could be resolved with this gradient would be about 0.25mm.

The gradients are quite linear with the shim setting as is shown in Figure II. The X and Y gradients being linear in this way means that the gradient direction can be conveniently varied by appropriate choices of the X and Y shim settings.

Encouraged by this result, I decided to attempt to reproduce the original Lauterbur experiment[1] with one slight twist - I wanted to find three capillaries instead of two. Thus, I added a third capillary to the NMR tube, placed the tube back in the magnet, spun it briefly so that I couldn't know where the capillary tubes were and began to collect views. A standard one pulse sequence was used with gradients taken along a variety of directions. I decided to take eight views (0, 30, 45, 60, 90, 120, 135, 150°), these angles being chosen because I knew the sines and cosines by heart. Each projection was hand digitized, fifteen intensities being obtained for each one. The image obtained from a simple back calculation of these projections is shown in Figure III along with a few of the projections themselves. Clearly the three capillaries in this phantom are found quite nicely. As it turned out, four views (0, 45, 90, 135°) were sufficient to produce an image similar to that in Figure III.

Finally I wanted to see whether or not I could demonstrate NMR contrast enhancement using the relaxation agent, GdDTPA. This is essentially the same experiment as that reported by Lauterbur in the second part of his paper except that Mn was used as the paramagnetic ion. I prepared two capillaries containing 50% H_2O/D_2O and two other capillaries 0.002M GdDTPA in 50% H_2O/D_2O. This solvent system was chosen in order to facilitate shimming. I attempted to shuffle the capillaries so that I wouldn't know which was which, but in the process I dropped them. None of them were broken, but now I <u>really</u> didn't know which was which. I collected them all and placed them in a 5mm NMR tube. Again I took eight views using a standard pulse sequence and a long delay (>30 sec) between acquisitions. The back projection calculation of this set of data is shown in Figure IVa. Note that there is a suggestion of the presence of four tubes, but I couldn't find a threshold that would show all four of them as resolved peaks.

Next I repeated the experiment, preceding the acquisition pulse with eight dummy pulses separated by no delay other than acquisition time. This experiment would be expected to discriminate against the capillary tubes containing no Gd salt. Back projection of this data set gave rise to the image in Figure IVb. This so-called T_1 weighted image shows only the two capillaries containing GdDTPA.

I then went back to the data shown in Figure IVa. By taking contours at the highest intensity in this data set I could find the other two capillaries (Figure IVc), the ones without Gd. This amounts to the production of a poor man's T_2 weighted image, one which discriminates against the capillaries containing the paramagnetic salt. Of course, I could go back, in principle, and collect spin echo data in order to get the same image, but, frankly, I was getting a little tired of collecting projections which then had to be analyzed by hand.

Honesty compels me to point out that because Gd is a chemical shift reagent, discrete spectra were observed for the Gd containing and Gd absent capillaries. However, prior to carrying out the back projection calculations the Gd capillary spectra were digitally shifted by the amount of shift observed in the absence of a gradient. Such small shifts as those observed here (0.4ppm) would not be observed on a clinical NMR imager having intrinsic linewidths of several ppm.

Thus it appears that it is indeed possible to carry out simple imaging experiments using an unmodified commercial high resolution NMR spectrometer. The data obtained from such experiments is suitable as a demonstration of one type of NMR imaging. In addition, such efforts serve to force one to take a closer look at the mathematics of back projection.

Sincerely,

C. Anderson Evans
Staff Scientist,
Analytical

[1]P. C. Lauterbur, *Nature, 242*, 190 (1973)

Figure I

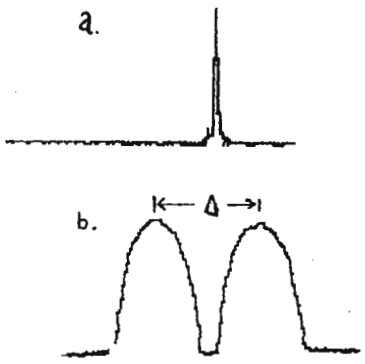


Figure II

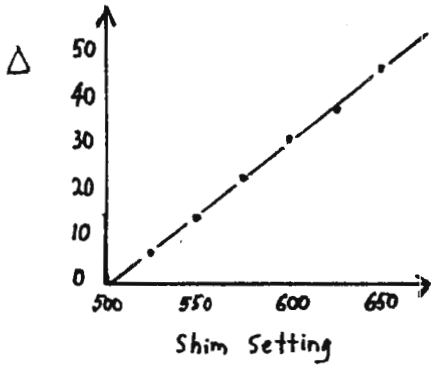
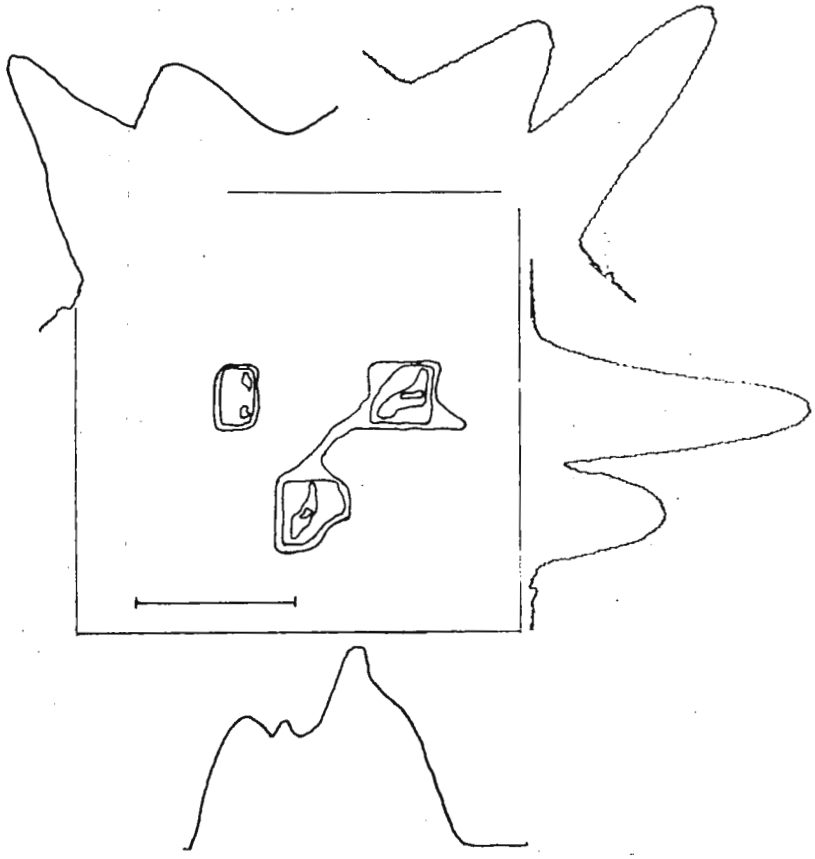
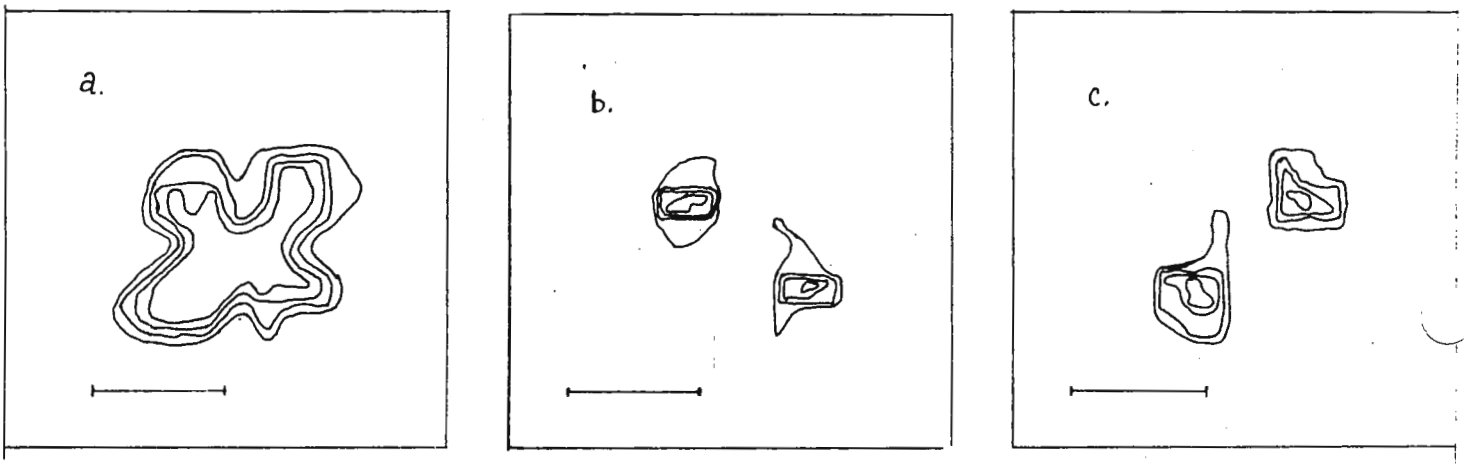


Figure III



*N. B. – The bar in each of the image displays corresponds to 2 mm.

Figure IV



How to bring true computer power to your NMR research

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

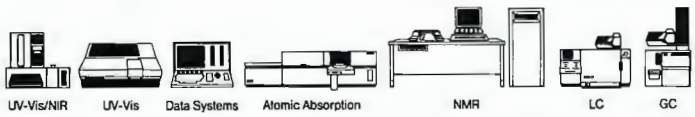
Now, for the first time, you can add a broad range of true computer capabilities to your NMR research. These features make that possible:

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

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

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

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



INTELLIGENT SOLUTIONS FOR YOU

varian

MAG-4615/338

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

Gemini

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

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

Never has FT NMR been this reliable

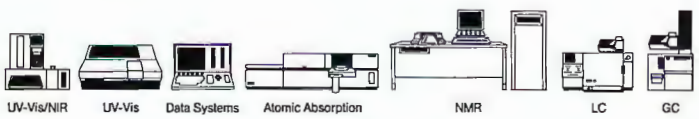
Gemini's industry-standard design, the complete automation of all spectrometer functions, user-proven expert system software and extensive diagnostics all combine to produce the world's most reliable FT NMR results.

Call now

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

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

Now available at 200 & 300 MHz!



INTELLIGENT SOLUTIONS FOR YOU

varian

SYRACUSE UNIVERSITY
NMR and DATA PROCESSING LABORATORY
GEORGE C. LEVY, DIRECTOR (315) 423-1021

DEPARTMENT OF CHEMISTRY, BOWNE HALL, SYRACUSE UNIVERSITY, SYRACUSE, N.Y. 13244-1200

March 25, 1987 (Received 26 March 1987)

Mr. Barry Shapiro
TAMU NMR Newsletter

NMR DATA PROCESSING WORKSHOPS IN BOLOGNA, ITALY; ZÜRICH, SWITZERLAND, AND LONDON, ENGLAND MAY AND JUNE, 1987

Dear Barry:

Three one-day seminar Workshops on NMR Data Processing will be held this May and June in Europe and England. The Workshops will include discussions of current and prospective NMR Data Reduction Methods, computer hardware technology, spectral optimization software, laboratory networking and NMR expert systems. Demonstrations will be conducted on advanced NMR workstation computers, although attendance at the practical demonstrations must be limited due to availability of a single computer at each Workshop. All three programs will be conducted by me, with some local participation. The three sessions are scheduled for:

Zürich, Switzerland, Laboratory of Professor Richard R. Ernst
Bologna, Italy, CNR Laboratory, Dr. Derek Jones
London, England, University of London, Birkbeck College, Dr. D.B. Davies

There will be no charge for attendance at these seminars. Please contact the local host directly for further information or to reserve a place:

Professor Richard Ernst
Laboratory fur Physikalishe Chemie
Laboratory 22
ETH-Zentrum
8092 Zürich Switzerland
Switzerland Phone 1-256-43-66
USA Phone 011-41-287119-00

Dr. D. B. Davis
University of London
Birkbeck College
Malet Street
London WCIE 7HX
England
USA Phone 011-44-1631-6253

Dr. Derek Jones
CNR Instituto Composti Carbonio
Via Tolara di Sotto, 89A
40064 Ozzano Emilia
Bologna, Italy
USA Phone 011-39-51-799-425

Dates of Workshops:

Zurich - May 25, 1987
Bologna - June 2, 1987
London - June 18-19, 1987

Best regards,

George C. Levy

George C. Levy
Science & Technology Professor

INSTITUT FÜR PHYSIK DER UNIVERSITÄT BASEL
EXPERIMENTELLE KERNPHYSIK
Klingelbergstrasse 82, Telefon 061 - 44 22 80
Prof. Dr. P. Diehl

CH-4056 Basel (Schweiz), 5.3.1987
(Received 10 March 1987)

Prof. B.L. Shapiro
Dept. of Chemistry
Texas A and M University
College Station, Texas 77843
U S A

"How important are the corrections for correlated deformation in structure determination of partially oriented molecules?"

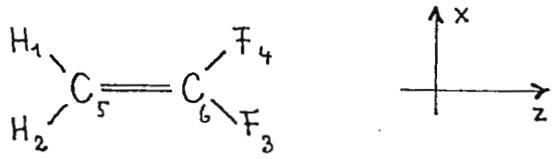
Dear Barry

Many experiments have shown, that the solvent dependence of structures derived from partially oriented solute molecules is due to the anisotropic interaction with the liquid crystal solvent inducing torques on the individual bonds which deform and simultaneously orient the solute. The effect can also be described as a correlation between the solute reorientational and vibrational motions. It is well known that vibrational motion considerably affects the direct couplings which must be corrected in order to derive a consistent structure. It is not so well known that correlated deformation may affect the direct couplings as much as or even more than harmonic vibration. As an example we have studied the molecule 1,1-difluorethylene. In the table we present the measured direct couplings without corrections, the vibration corrections and the deformation corrections together with the corresponding structure results. It can be seen, that the correction for deformation in D_{12} exceeds the one for harmonic vibration. Obviously deformation corrections must be applied in general. We are therefore developing a computer program for this purpose.

Yours sincerely

P. Diehl R. Wasser

Table: Measured direct couplings of 1,1 - difluoroethylene, 1 atm. in EBBA, corrections for harmonic vibration as well as for deformation and corresponding structure results. T = 303 K.



	D_{exp}	D_{harm}	D_{def}
D_{12} (Hz)	- 24.82	7.39	12.5
D_{13}	- 75.02	0.62	0.36
D_{14}	-236.30	-0.22	-0.18
D_{15}	-209.96	32.52	17.15
D_{16}	- 99.87	2.62	-0.18

	uncorr.	corr. for vibr.	corr. for vibr. and def.	MW
r_{15}/r_{56}	0.905(7)	0.833(6)	0.807(3)	0.814(8)
r_{36}/r_{56}	1.041(3)	1.106(2)	0.999(11)	0.981(5)
$\measuredangle$ 156(°)	119.3 (2)	119.3 (2)	122.2(1.5)	122.0 (8)
$\measuredangle$ 564	104.4 (3)	108.1 (3)	110.0 (7)	110.6 (6)
r_{15} (Å)	1.189(9)	1.095(7)	1.062(6)	1.071(11)
r_{46}	1.368(3)	1.335(3)	1.32 (5)	1.291(6)
S_z	0.0429	0.0384	0.0362	
S_x	0.0018	0.0019	0.0024	

ABBOTT

Abbott Laboratories
North Chicago, Illinois 60064

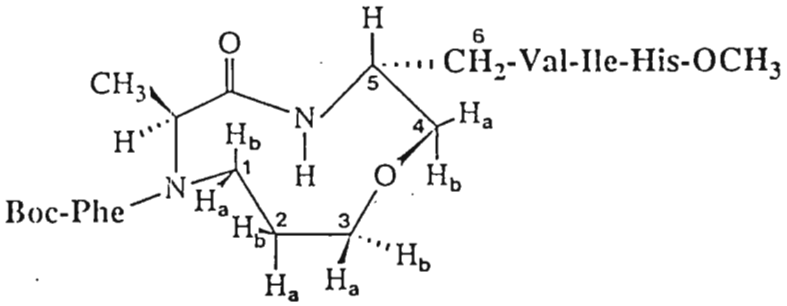
March 9, 1987 (Received 23 March 1987)

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

Dear Professor Shapiro:

RE: Circular Analysis of a Cyclic Peptide

Recently, we completed a detailed conformational study of a cyclic peptide, **1**, to determine if its inability to inhibit human renin could be attributed to its conformational properties.



1

The 2D NOE spectrum of **1** was ideal for quantitative evaluation of the NOEs. Almost all of the crosspeaks were well resolved and thus, after baseline correction in ω_1, were amenable to accurate integration. Despite the 4 methylene groups and ether linkage contained in the cyclic portion of the peptide, our NMR results indicated a preferred conformation for the macrocyclic ring of the peptide (more details to appear in Biochemistry, April 1987).

The agreement of the NMR data with a single structure tempted us to make a direct comparison of the experimental NOE data to simulations based on the structure determined from the NMR data. This comparison is shown in Figure 1.

The agreement between the experimental data and the simulations are quite acceptable when one considers that a small difference (0.2A) in the interproton distance is easily seen in the initial slope of the NOE time development. The simulated curves do a fair job over the entire time course of the measured time developments. This indicates that relaxation rates other than the interproton sigma are also adequately accounted for by the structure.

Sincerely,

S. Fesik R. Gampe D. Nettesheim E. Olejniczak E. Zuiderweg

S. Fesik, R. Gampe, D. Nettesheim, E. Olejniczak, E. Zuiderweg

/cd

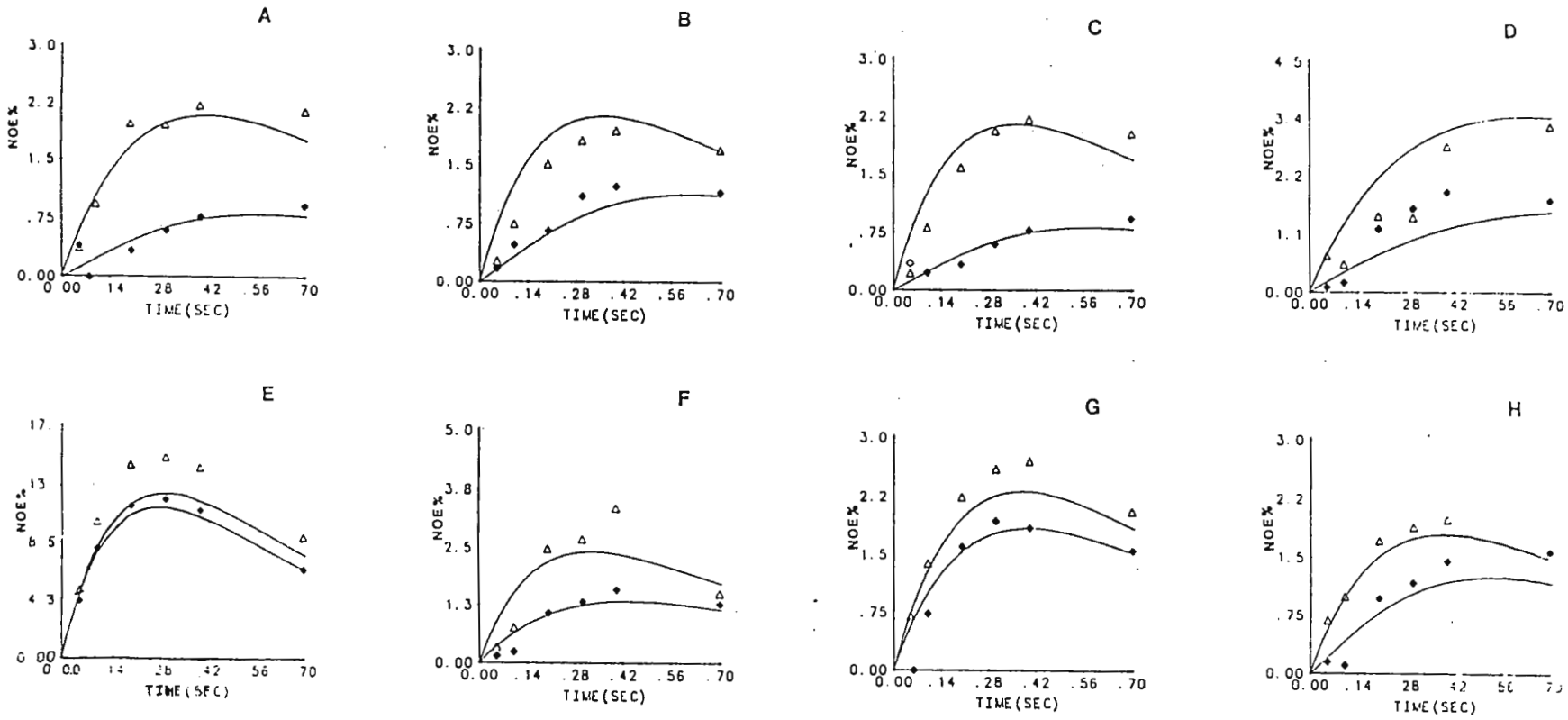


FIGURE 1 CAPTION

COMPARISON OF EXPERIMENTAL 2DNOE DATA TO SIMULATIONS BASED ON THE THREE DIMENSIONAL STRUCTURE OF COMPOUND I.

FIGURE	OPEN TRIANGLES	FILLED DIAMONDS
A	TOP CURVE 1A – 2B	BOTTOM CURVE 3B – 4A
B.	TOP CURVE 1A – 2A	BOTTOM CURVE 4A – 6A
C	TOP CURVE 1B – 2B	BOTTOM CURVE 3B – 4A
D	TOP CURVE 4A – 5	BOTTOM CURVE 4B – 5

FIGURE	OPEN TRIANGLES	FILLED DIAMONDS
E.	TOP CURVE 1A – 1B	BOTTOM CURVE 2A – 2B
F.	TOP CURVE 3B – 4B	BOTTOM CURVE 3A – 4B
G.	TOP CURVE 2A – 3A	BOTTOM CURVE 2B – 3A
H.	TOP CURVE 2A – 3B	BOTTOM CURVE 1B – 2A

Research Centre
P.O. Box 5000
Kingston, Ontario
Canada. K7L 5A5

DU PONT CANADA INC.

March 9, 1987
(Received 17 March 1987)

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

MEASURING TEMPERATURE IN ^{13}C CP/MAS NMR

Dear Barry:

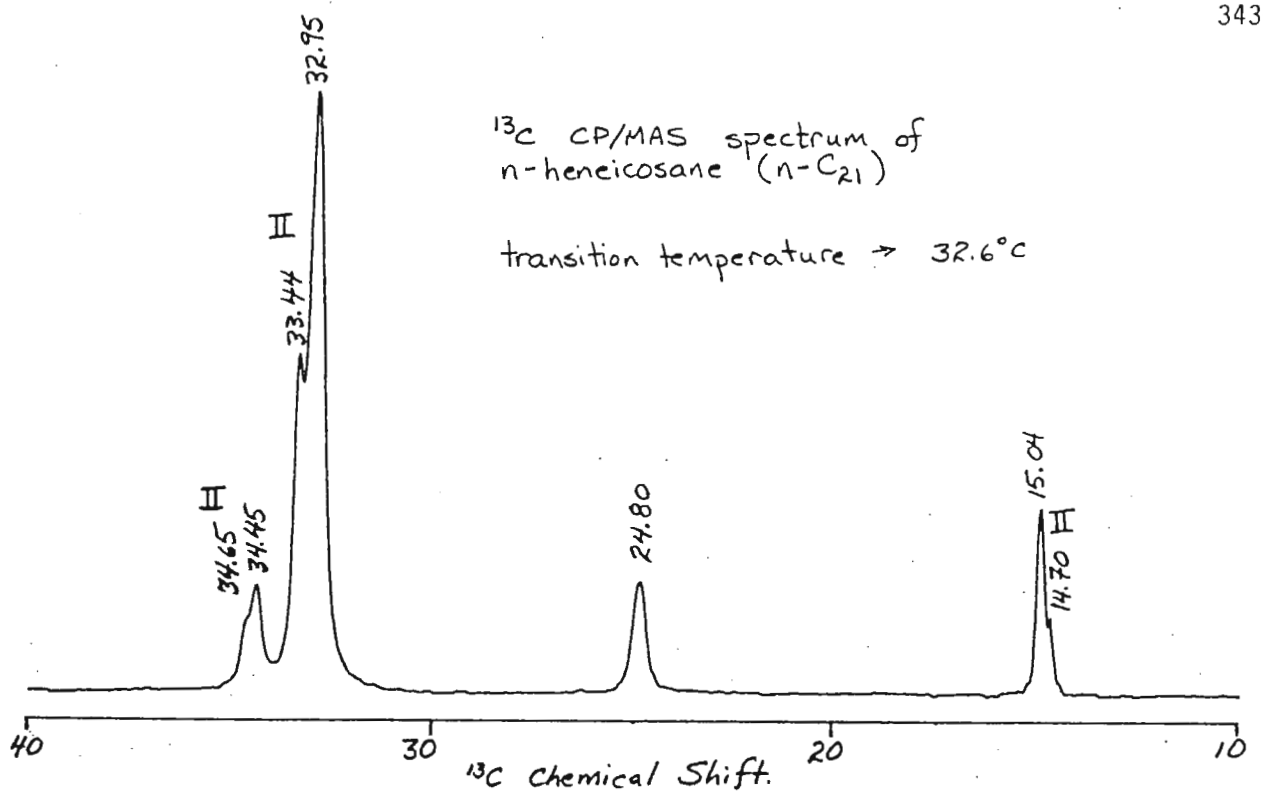
Recently, R. Crandall and S. Kaplan (TAMU note 341-4) have described problems in the use of samarium acetate tetrahydrate as a thermometer for ^{13}C solid state NMR experiments at temperatures above 25°C. As an alternative to an internal chemical thermometer, we have been using the phase transitions of odd numbered, n-alkanes to calibrate our Bruker B-VT 1000 to the actual temperature inside the MAS rotor.

The odd numbered n-alkanes ($9 \leq n \leq 45$) undergo a variety of different solid-solid phase transitions prior to melting (see references 1 and 2 for transition temperatures). However, for all of the alkanes, the last solid-solid transition is to a pseudohexagonal ($9 \leq n \leq 21$) or hexagonal ($21 < n \leq 45$) packed structure called phase II. In this phase the chains are able to undergo large amplitude jumps about their long axis and there is conformational disorder present. Since this transition to phase II is very abrupt (0.2 - 0.4°C) and since there is as much as a 0.5 ppm change in the chemical shifts of the methyls and the central methylenes during the transition, we have used this transition to calibrate our temperature controller. The onset of the transition by ^{13}C CP/MAS NMR has been compared to the DSC derived values to give a correlation of the controller set point to the actual sample temperature. This technique also allows us to quickly and easily examine the effect of gas flow rates (spinning speed) and the time required for the sample to reach an equilibrium temperature within the rotor. The uniformity of temperature throughout the sample can also be examined (see Figure 1). At this controller setting approximately 30% of the sample is in phase II while 70% is in an orthorhombic phase, indicating that despite a 30 minute equilibration time, there is a temperature gradient of at least 0.4°C across the sample.

While we have not examined all of the n-alkanes which undergo this transition, those we have examined have shown abrupt transitions by NMR, provided the alkanes are suitably pure (> 99.5%) and one has sufficient resolution to measure the chemical shift change.

Eric

Eric Kelusky



^{13}C CP/MAS spectrum of n-heneicosane (n-C_{21})

transition temperature → 32.6°C

1. M. Maroncelli, S.P. Qi, H.L. Strauss and R.G. Snyder, J. Am. Chem. Soc., 104, 6237-6247 (1982).
2. M.G. Broadhurst, J. Res. Natl. Bur. Stand., Sect A, 66, 241 (1962).

The British Petroleum Company p.l.c.

BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN

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

Our reference	Your reference	Telephone Sunbury-on-Thames	Date
S/SYB/57/87		(0932) 76 2622	12th March 1987
			(Received 20 March 1987)

Use of an External Computer for Spectrometer Control and Data Manipulation

Dear Professor Shapiro,

We are interested in performing relaxation and diffusion measurements on a variety of systems, for which we have a Bruker CXP100/Aspect 2000 spectrometer. A bit-mapped display is not supported on this sytem however, which, together with the lack of time domain software, makes the fitting and display of relaxation data difficult. An additional requirement is the automatically control of external equipment. For these reasons, we have decided to use an external computer (HP 320) to control the CXP and external hardware, and manipulate the data collected.

The control of the CXP by the HP 320 is simple to implement. The HP is connected to serial port A on the Aspect 2000 instead of the silentype terminal (see figure) and a simple terminal emulator program on the HP handles the input/output to this port. This is equivalent to connecting any video terminal to port A on the Aspect 2000.

In order to fit the data collected by the CXP, it needs to be transferred from the Aspect 2000 to the HP. This data transfer can be done in ASCII format using 'BEAM', but this is slow and has no error checking. We preferred to use the DISCXP command 'TRSB' to transfer data over serial port B. This uses the 'specnet' protocol, and so a specnet handler routine needs to be written for the HP in order to transfer the data. Additional routines are also needed to convert data into the format required by the HP. This approach has the advantages of being faster, more robust as an error-checking scheme is used in 'specnet', and is directly accessible from DISCXP.

The transferred data can be fitted on the HP using standard procedures and high-quality output obtained from a digital plotter.

Registered office.
Britannic House
Moor Lane
London EC2Y 9BU

Registered in England
No: 102498

Telephone (switchboard)
Sunbury-on-Thames
781234

Telex 296041
(A/B BPSUNA G)

Facsimile No:
Sunbury-on-Thames
762999 (G1, 2, 3)

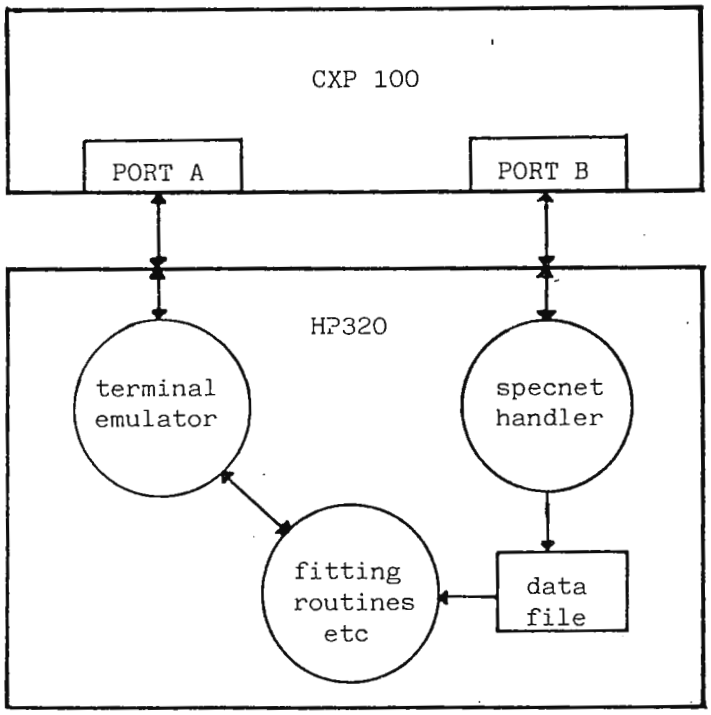
This strategy was initially implemented under the HP Pascal Operating System, and worked very well. Control of the CXP, data transfer and fitting could be done from within a single program on the HP, looking like an enhanced DISCXP program to the user. The fitting procedures showed a speed improvement of about 300 compared to an almost identical routine written in Pascal on an MSL100. Typically, fitting of a large data set to a multiexponential decay function takes of the order of one minute on the HP compared with several hours on the Aspect 3000.

We have recently increased the versatility of this approach still further by upgrading the operating system to multiuser UNIX. This allows the manipulation of data by a person other than the CXP operator, and makes the addition of further facilities straightforward

Yours sincerely,

P.A. OSMENT
Spectroscopy Branch

PS. Please credit this contribution to Ken Packer's account.



The interfacing of an HP320 to the Aspect 2000 computer of a Bruker CXP spectrometer, showing control and data transfer.

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

Telephone: (312) 972-3524

March 17, 1987
(Received 23 March 1987)

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

RE: Chemical Constitution of Synthetic [^{13}C]Lignins

Dear Barry:

Recently, we have been able to prepare synthetic lignins by enzyme-controlled oxidative coupling of [^{13}C]coniferyl alcohols. Our interest in 'polymer models' for natural lignins arises from their potential use in ^{13}C-labeling experiments to examine chemical transformations of lignin during coalification. In this letter, I describe the characterization of these synthetic polymers by solid ^{13}C NMR, and discuss their structural similarities and differences to natural softwood lignin.

The cross polarization/magic-angle spinning (CP/MAS) ^{13}C-NMR spectrum of unlabeled, synthetic lignin shows a remarkably close correspondence to that obtained for a natural softwood lignin sample. The spectra of both samples are characterized by a sharp absorption band centered at 55 ppm for the methoxyl carbons, a reasonably broad resonance at 120-140 ppm for aromatic carbons and an intense, narrow band at 155 ppm typical of phenolic carbons. A shoulder appearing to higher field of the aromatic carbon absorption (~115 ppm) is indicative of aromatic carbons ortho to phenolic groups. In addition, there are less intense resonances which appear in the aliphatic region (0-45 ppm) and an absorption of low intensity centered at 85 ppm, which is consistent with α- and β-aryl ether groups.

The CP/MAS ^{13}C-NMR of 45% enriched [β-^{13}C]lignin produces a spectrum, shown in Figure 1, in which the signal from the ^{13}C-labeled carbons is considerably intensified compared to those with the natural ^{13}C abundance. Because its NMR spectrum is considerably less complex than the unlabeled sample, it is possible to assign the major structural subunits which characterize the synthetic lignins. An inspection of the spectrum reveals that β-O-4 aryl-alkyl ether structures centered at 85 ppm and β,β-resinol structures at 54 ppm are predominant, whereas dihydrofuran (phenylcoumaran) structures at 45 ppm are present in smaller amounts. Moreover, the presence of coniferyl alcohol end groups is indicated by the intense resonance centered at 128 ppm.

Previous studies on the structure characterization of natural lignins suggest that almost all C_β atoms are involved in inter-subunit bonds. A comparison of the distribution in common β-carbon linkages found in softwood lignins with the distribution determined by NMR analysis of the synthetic lignins is presented in Table 1. The relative intensities of resonances in the spectrum of [β-^{13}C]lignin have been measured to determine the distribution of β-carbon linkages in the synthetic lignins. The ratios for β-O-4 aryl-alkyl ether

and β,β-resinol structures were then used in conjunction with the integrated intensity of the 85 ppm region in the spectrum of unlabeled synthetic lignin to provide the results shown in the Table. It is seen that substantially fewer β-O-4 aryl-alkyl groups and approximately 3.5 times the number of coniferyl alcohol end groups are found in the synthetic polymers.

TABLE 1. Frequency of Common β-Carbon Linkages Found in Softwood and Synthetic Lignins.[a]

Linkage	Softwood Lignin[b]	Synthetic Lignin[c]
β-O-4 Aryl-alkyl ether	5.0 - 5.6	3.0
β, β-Resinol	1.9 - 2.5	2.5
Phenylcoumaran	1.0 - 2.2	1.6
Coniferyl alcohol end groups	1.0	3.5

[a]Expressed as percentage of total number of carbon bonds.
[b]Range of values converted from data compiled in the literature.
[c]This work.

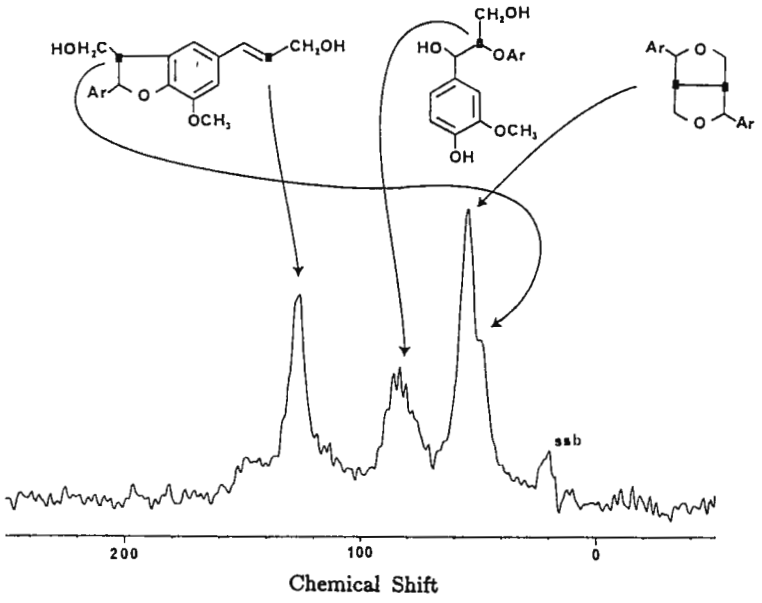


Figure 1. CP/MAS ^{13}C-NMR spectrum of 45% enriched [β-^{13}C]lignin. Structures designated from left to right are dihydrobenzofuran(phenylcoumaran), β-aryl ether and β,β-resinol subunits, where Ar represents a 4-hydroxy-3-methoxy-phenyl group.

Sincerely,

Robert E. Botto
Chemistry Division

Wellcome

The Wellcome Research Laboratories
The Wellcome Foundation Ltd.
Langley Court
Beckenham
Kent BR3 3BS

telephone 01-658 2211
telegrams and cables
WELLAB BECKENHAM
telex
WELLAB
BECKENHM 23937

1985

BMNC/87/3

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

17th March 1987

(Received 24 March 1987)

Dear Professor Shapiro,

"SUMMON UP THE BLOOD" [1]

Donated blood stored in the usual way in bags ready for transfusion gradually loses its capacity to deliver oxygen to tissues because the level of bis-2,3-diphosphoglycerate (BPG) in the blood decreases with time due to metabolism, eventually to inorganic phosphate (P_i) and lactate. BPG is the substance which stabilises the deoxy form of haemoglobin by binding to it causing an allosteric lowering of its affinity for oxygen, and hence promoting oxygen delivery. Thus any compound which raises the level of BPG in stored blood compared to a control of the same age ex vivo has potential for improving the quality of the blood immediately post transfusion when the patient is usually most hypoxic [2].

We have been using ^{31}P NMR to monitor the BPG level in stored blood taking aliquots at weekly intervals and a typical spectrum is shown in the Figure. (a) represents fresh blood and (c) is from an aliquot taken from the same sample three weeks later. The BPG level has decreased substantially and the inorganic phosphate increased. (b) shows the spectrum from three week old blood to which had been added, at day zero, a compound [3] which was expected to increase the BPG level over control. It is not possible to simply add extra BPG as it does not penetrate into red blood cells. Clearly the compound, BW A440C, has caused the BPG loss to be slowed down significantly (such that after three weeks the BPG level is about that after a few days in control blood).

The ^{31}P NMR analysis is straightforward, being carried out at 145 MHz on a Bruker AM-360 using 2 ml of blood in a 10 mm tube at 37°C. Estimation of pH has also been achieved based on the P_i chemical shift.

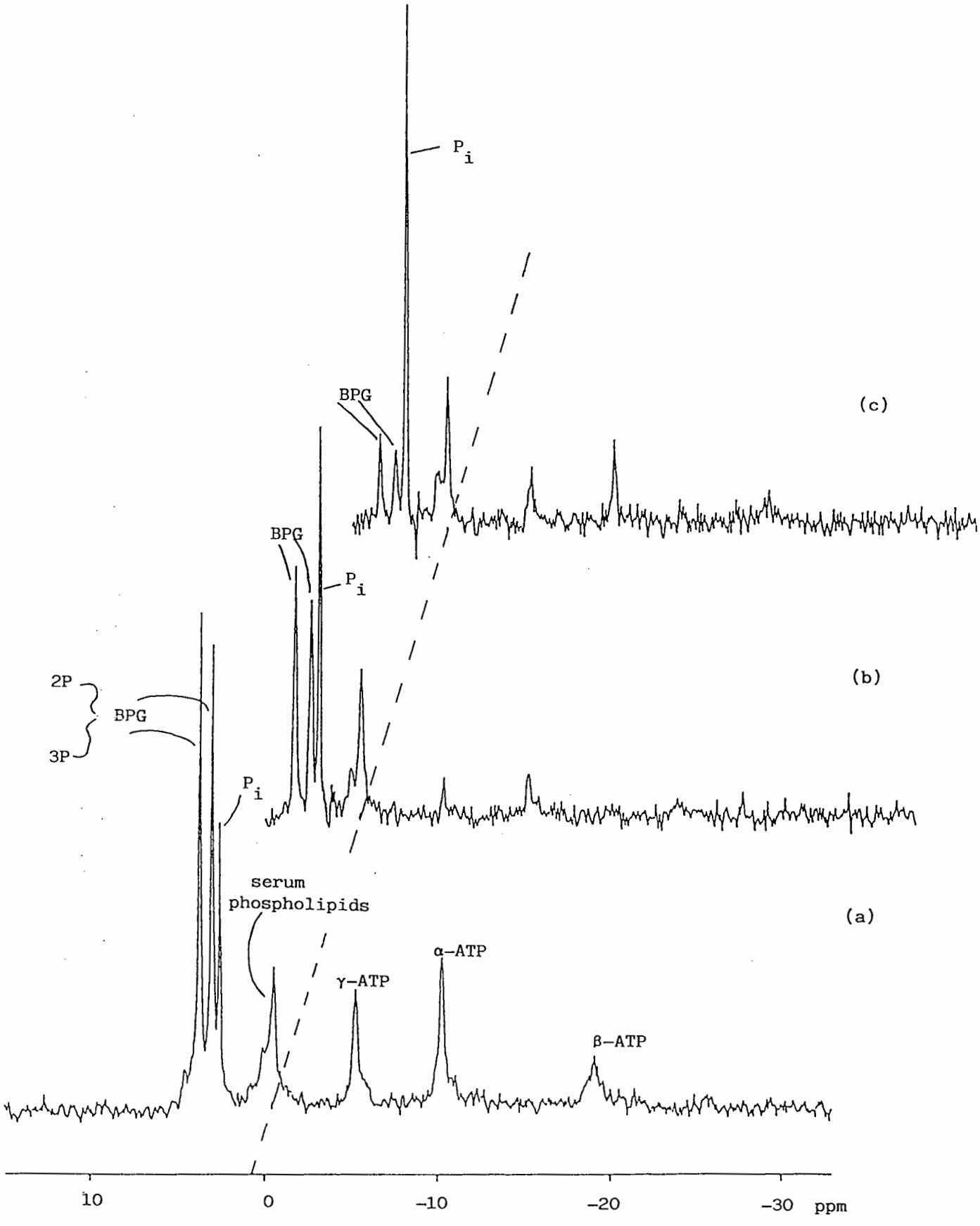
Yours sincerely,

John Dorothea

J.C. LINDON D.J. BAKER
Department of Physical Chemistry

[1] W. Shakespeare, Henry V, Act II.
[2] R.M. Hyde et al, Lancet, ii, 15-16 (1984)
[3] R.A. Paterson et al, Transfusion, in the press (1987)

Enc.


P i
BPG
(c)
BPG
P i
2P
BPG
3P
(b)
P i
serum
phospholipids
(a)
α-ATP
γ-ATP
β-ATP
10
0
-10
-20
-30
ppm

Warner-Lambert Company
Pharmaceutical Research Division
2800 Plymouth Road
Ann Arbor, Michigan 48105
313 996-7000

WARNER LAMBERT

March 18, 1987 (Received 24 March 1987)

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

Dear Professor Shapiro:

PARKE-DAVIS PHARMACEUTICAL'S LAB: AN INTRODUCTION

Our laboratory is presently pursuing a variety of NMR related projects. In addition, we provide a number of routine analytical services to support the ethical drug discovery program.

One area of considerable interest to us has been the development of a specialized data processing, archiving, and retrieving system to improve sample throughout and record keeping. Customized programs are used to transfer data from various instruments (NMR, MS, and IR) to remote data processors. Sample tracking is performed on the remote processors and then the spectral data is transferred to our IBM 3083 mainframe computer where it is archived. Laboratory chemists use other programs and utilities to sift through the mainframe spectral database and perform additional data processing and output when desired. The system has allowed us to mostly eliminate hardcopy spectral files and microfiche. Naturally, we also benefit from increased utilization of our instruments for the collection of spectral data.

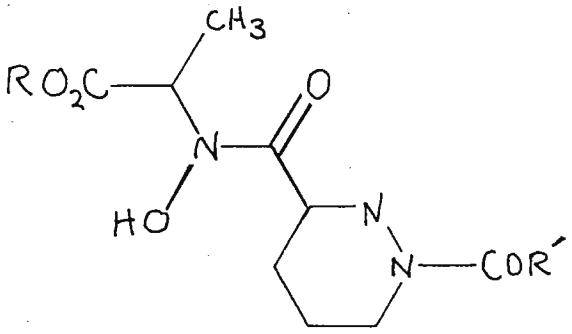
A new peptide antibiotic was isolated recently by our fermentation chemists. X-Ray data, provided by Jon Clardy and co-workers, Cornell, and NMR data reveal several interesting features for the natural product. It is a cyclic depsipeptide consisting of five amino acids, two of which are hexahydropyridazine carboxylic acid analogs. The peptide also contains a N-hydroxyalanine amino acid which seems quite rare. We are continuing our investigation of this peptide by using molecular modeling in concert with NOE and structure data to resolve the minimum energy solution conformation.

We were overjoyed to discover that Varian has written a program to interactively add and subtract spectra for their latest 6.1 version software. Our laboratory uses the NOE difference technique quite often for routine structure elucidation and conformational analysis. The method was often quite difficult to apply when used with the old (ADD SUB etc.) non-interactive utilities supplied by Varian. One of us (CR) was busy writing an interactive version and will now turn toward some other software need. Perhaps the file and directory management program, MANAGR, should be dusted off and reconsidered. We will report on our success and application of these projects in our next letter.

Sincerely,

Chris Rithner, Ph.D. Ms. Susan Uhlendorf Ms. Diana Omecinsky

CR:cc/056



N-hydroxyalanine and
hexahydropyridazine moeity

Brandeis University

Graduate Department of Biochemistry
Waltham, Massachusetts 02254-9110

March 20, 1987 (Received 26 March 1987)

Prof. Barry Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Running a Home-Brew 500 MHz. NMR Spectrometer With an IBM AT Clone

Dear Barry:

Recently I've converted our home-brew 500 MHz instrument to be run by an IBM AT clone. This was relatively simple because the spectrometer was previously run by a multibus CP/M computer using the precursor to the AT's chip set (8086/87) so that all I had to do was adapt the previous mature program to the slighlty differing I/O of the AT and of MS/DOS. This conversion was made to avoid likely maintainance problems and certain obsolescence of our old computers.

There were more difficulties than I expected, too boring to mention here, but they were overcome and the system now works perfectly. The program is based on "small model" "C" language and currently is about 40 KB in length, with another roughly 40 KB for cosine and other tables. There are separate programs for 2DFT and 2d display.

Very large data sets, up to around 450 KB, are manipulated by a relatively few assembler programs that receive pointers to blocks of data in the form of paragraph adresses only, as segment pointers. FT and display programs are also assembler programs that use the same pointer system. Complex one-D FT,s of up to 32K 32 bit points can be handled, using DS (data segment) as the base for real data and ES (extra segment) for imaginary (always, here, "points" means twice the number of complex points). Larger FT's could be performed with only a little more programming and no great time-inefficiency.

This system is so inexpensive that I could immediately afford a second one as a data station. The data station has EGA color and both systems use Houston DPM 40 plotters which are slow but inexpensive and reliable.

The 2D FT program takes 8-10 minutes to read and process a 480*512 point 32 bit data set on hard disc and finish with an output file on the hard disc. Only about 20% of the time is used for disc I/O, mainly because I use the semtransposed intermediate storage method I described in JMR 52, 310 (1983). The clock is 6 MHz for the 80286 and 4 MHZ for the 80287, and the hard disc is a 40 ms access Seagate. Installation of a 10 MHz 80287 (from Microway) incrreases speed by only about 20%, but I believe that if both clocks were 10 MHz the time might be cut in half. To process such a data set takes 864 FT's of 1024 points, each of which includes 2x zerofill, multiplication by an arbitrary weighting function, and phase and amplitude correction of any form. 2d data size is limited only by the hard disc size.

I wrote this FT program when I needed it for my previous system and could find no commercial or other program for the 8087, but it still may be unsurpassed for speed. It makes maximum use of the two processors by using the coprocessor only for multiplication, and doing absolutely all additions as 32 bit integers outside the coprocessor. Further, all multiplications using the same magnitude of sine and cosine are grouped together to minimize loading them into the coprocessor. This strategy is optimum because it takes about an equal amount of time to load a floating point integer as it does to convert and load a 32 bit integer, and a similar time is needed for multiplication. Also, the '86 is pretty good at adding long integers, and integer arithmetic is really adequate for FT in which small numbers never get blown up to be big. I get extra dynamic range by shifting the data right 3 bits, after 8 groups of butterflies, which only throws out accumulated roundoff errors. This program is available from me unsupported with existing poor documentation.

The design of the instrument's program is vastly simplified by the existence of the autonomous input processor/memory built by Sara Kunz (Rev. Sci. Instrum. 54, 503 (1983)). This distantly resembles the one on Varian instruments, but is better because it is much simpler so that it isn't as busy and can survive complete replacement of the computer, as it just did. It now has a 14 bit A/D. Transfer of 4 accumulated 1K FID's to the AT takes about 0.1 sec with error checking. The timer system is also autonomous but I can't say that it is so great; it is now being upraded using field-programmable logic. Most of the time the instrument computer does nothing because the input processor and timer are doing all the work. It could easily time-share 2D processing with a 2D run to give an update on signal/noise, or do word processing while taking data (except that that would violate NIH rules).

I do not claim that the AT-class of computer is more cost-effective than some other type for which NMR program support exists. Much of what I have said about speed could be viewed as irrelevant since inexpensive array processors are available. I guess the main message is to plan for obsolescence; and if so, inexpensive may be good. The instrument's computer can be obtained for between $2500 and $4000 with hard disc and the data station's computer costs around $800 more because it has a color display (EGA) and 30 MB disc. These computers will be obsolete long before my 500 MHz magnet is, but the program is likely to be compatible with the next generation of computers already being developed.

Sincerely,

Alfred Redfield

Alfred G. Redfield
Department of Biochemistry
Brandeis University
Waltham, MA 02254, USA

343-50

BLUE HEN NMR COMPLEX

CHEMISTRY DEPARTMENT
UNIVERSITY OF DELAWARE
NEWARK, DELAWARE 19716
(302) 451-2739

23 March 1987
(Received 26 March 1987)

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

(1) Proton Exchange of Labile Deuterium in Trifluoroethanol-d_3
(2) Blue Hen NMR Symposium

Dear Dr. Shapiro,

Trifluoroethanol (TFE) has been chosen as a solvent for NMR investigations for a number of biologically interesting peptides.[1,2] This is due to its structure-promoting ability, in particular its stabilization of helix.[3] We wish to communicate a simple procedure for preparing TFE-d_2 by exchanging the labile ^2H for ^1H from ethylene glycol.

Prior to the conformational analysis of small, 9-26 residues, linear peptides by NMR, we use circular dichroism (CD) to determine bulk secondary structural characteristics using aqueous buffers, polyfluoro alcohols, ethylene glycol, and SDS micelles. We have used CD to characterize the secondary structural preferences of a set of peptides from Salmonella phage P22 tail spike protein that are proposed to play a critical role in initiating folding of the tailspike protein.[4] Trifluoroethanol promoted a helical conformation for a 22 residue peptide corresponding to residues 228-249 of the P22 tail spike protein. This sparked our interest in further characterization of the P22 tail spike peptides by NMR in TFE.

Trifluoroethanol is commercially available as TFE-d_3 98% atom D. A cursory search of Chemical Abstracts for NMR and TFE did not lead to a method of exchanging the labile deuteron for proton. We have obtained good yield (≥80%) of TFE-d_2 by a simple distillation of TFE-d_3 from ethylene glycol. Ethylene glycol was spectral grade (Aldrich) and TFE-d_3 was from Cambridge Isotopes. Typically we use 5 ml of ethylene glycol to 1 ml of TFE-d_3 in a 8 ml total capacity mini-still. The first fraction is collected over a temperature range of 72-80°C (uncorrected). The distillate is stored over 4A molecular sieves until sample prep.

This method has, at least, started our NMR experiments using TFE-d_2. We would be interested in learning other tried methods for exchanging ^2H for ^1H for alcohols in general.

One additional note, the Blue Hen NMR Symposium held annually at the University of Delaware will be the 1st of June 1987. Speakers this year include Eric Oldfield, Joanne Ingwall, Allen Garroway, Steve Fesik, and Jacques Fraissard. Those interested in further information can contact Dr. L. M. Gierasch at the above address.

Please credit this to Cecil Dybowski's subscription.

Sincerely,

Roger Crecely Cecil Dybowski Joe Noggle

Adam N. Stroup Lila M. Gierasch

1Mammi, S.; Goodman, M.; Peggion, E.; Foffani, M.T.; Moroder, L.; Wünsch, E. Int. J. Pept. Protein Res. 1986, 27, 145-152.

2Clore, G.M.; Martin, S.R.; Gronenborn, A.M. J. Mol. Biol. 1986, 191, 553-561.

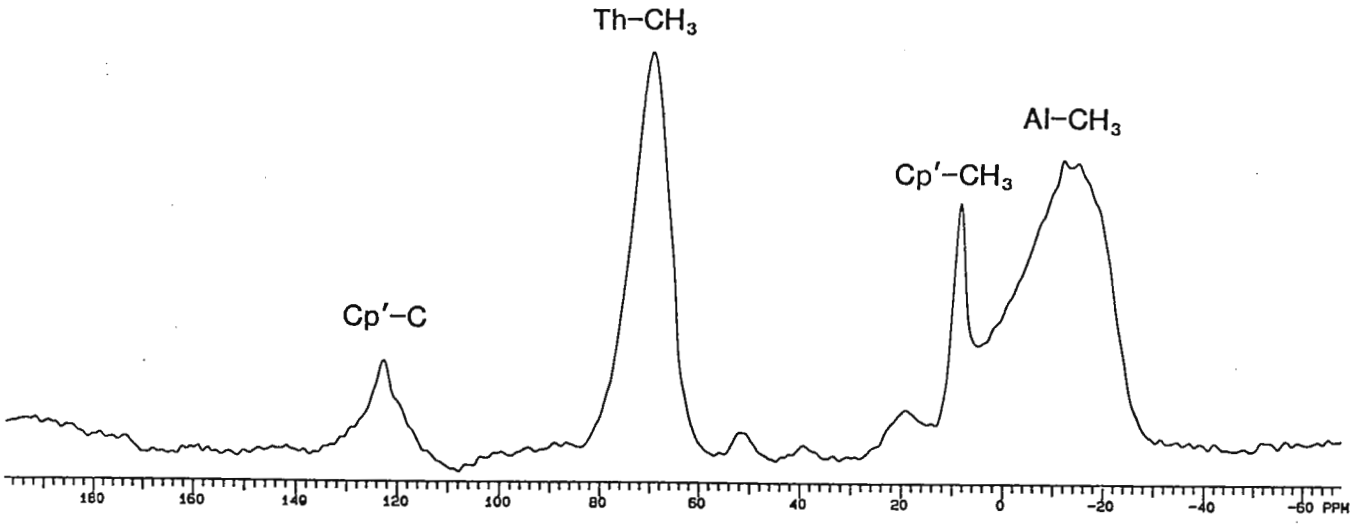
3Ebert, G.; Kuroyanagi, Y. Int. J. Biol. Macromol. 1983, 5, 106-110.

4Goldenberg, D.P.; Smith, D.H.; King, J. Proc. Natl. Acad. Sci. USA 1983, 80, 7060-7064.

(Continued from page 53)

^{13}C CPMAS Solid State NMR Spectrum of $Cp'_2Th(CH_3)_2$/DA

99% ^{13}C Enrichment at Th-CH_3



NORTHWESTERN UNIVERSITY COLLEGE OF ARTS AND SCIENCES

Department of Chemistry

2145 Sheridan Road
Evanston, Illinois 60201

March 23, 1987
(Received 26 March 1987)

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

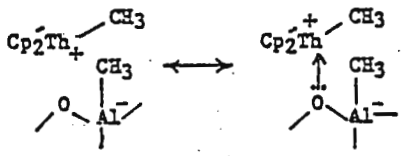
CPMAS STUDIES OF SUPPORTED ORGANOACTINIDE CATALYSTS

Dear Barry:

When adsorbed on high surface area inorganic supports such as dehydroxylated alumina and magnesium chloride, organoactinide molecules are highly active catalysts for olefin hydrogenation and polymerization (1). Moreover, the well-defined formal oxidation states (e.g., Th(IV) can't be oxidized and is exceedingly difficult to reduce) and other spectroscopic markers of organoactinides make them ideal models for technologically important early transition metal-support catalyst assemblies. Of course, elucidating the structure(s) of the organometallic adsorbates is of crucial importance.

We have found ^{13}C CPMAS spectroscopy to be an extremely powerful tool for probing the structures of adsorbed organoactinides and thus understanding the surface coordination chemistry (2). Since most of the supports have surface areas in excess of 150 m^2g^{-1}, spectra can be obtained at far less than monolayer coverage. An example would be our studies of $Cp'_2Th(CH_3)_2$ ($Cp' = \pi$-$(CH_3)_5C_5$) adsorbed on dehydroxylated alumina (γ-Al_2O_3 heated at 950°C and having ca. 5.5 surface O^{-2}, 5.5 surface Al^{+3}, and ca. 0.14 surface OH moieties per 100 $Å^2$). Spectroscopic assignments are based upon studies with $Cp'_2Th(CH_3)_2$, $Cp'_2Th(^{13}CH_3)_2$, $(Cp'_2ThH_2)_2$, and various model compounds. Additional structural/dynamic information is provided by dipolar dephasing, variable magnetic fields, variable contact times, cessation of dipole decoupling, and Bloch decay experiments. Our initial studies were performed with a rather limited JEOL FX-60QS spectrometer. The recent acquisition of a Varian VXR-300 instrument with Doty solids equipment has greatly enhanced our capabilities in terms of sensitivity, chemical shift dispersion, and experimental versatility. An example is the spectrum of $Cp'_2Th(^{13}CH_3)_2$/dehydroxylated alumina shown in the accompanying figure. Spectral assignments follow

from the experiments outlined above. A key observation is the transfer of a methyl group from thorium to the Lewis acid Al^{+3} sites on the alumina surface (A). The chemical shift of the residual



A

$Th-CH_3$ surface moiety and recently synthesized model compounds (3) argue that the surface organoactinide is an unprecedented cationic species.

Sincerely yours,

David Hedden
Postdoctoral Fellow

Tobin J. Marks
Morrison Professor of Chemistry

P.S. Please credit this contribution to Joe Lambert's account.

References

1. (a) He, M.-Y.; Burwell, R. L., Jr.; Marks, T. J. Organometallics 1983, 2, 566-569.
   (b) He, M.-Y.; Xiong, G.; Toscano, P. J.; Burwell, R. L., Jr.; Marks, T. J. J. Am. Chem. Soc. 1985 107, 641-652.
   (c) Burwell, R. L., Jr.; Marks, T. J. in Augustine, R. L., Ed. "Catalysis of Organic Reactions"; Marcel Dekker, Inc.: New York, 1985; pp. 207-224.
   (d) Xiong, G.; Burwell, R. L., Jr.; Marks, T. J., manuscript in preparation.
2. (a) Toscano, P. J.; Marks, T. J. J. Am. Chem. Soc. 1985, 107, 653-659.
   (b) Toscano, P. J.; Marks, T. J. Langmuir, 1986, 2, 820-823.
   (c) Hedden, D.; LeMarechal, J.-F.; Toscano, P. J.; Marks, T. J. Abstracts, 193rd ACS National Meeting, Denver, April 1987, INOR 404.
3. (a) Lin, Z.; LeMarechal, J.-F.; Marks, T. J. Abstracts, 193rd ACS National Meeting, Denver, April 1987, INOR 314.
   (b Lin, Z.; LeMarechal, J.-F.; Sabat, M.; Marks, T. J., submitted for publication.

343-54

RESEARCH SCHOOL OF CHEMISTRY

THE AUSTRALIAN NATIONAL UNIVERSITY

Telephone: (062) 49 3637 (School)
(062) 49 3771 (Direct)
Telex: AA62172
Fax: (062) 48 7817

G.P.O. Box 4
Canberra, A.C.T. 2601

5 March 1987
(Received 27 March 1987)

Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77343
United States of America

Dear Barry,

About two years ago the ANU set up a university-wide NMR centre, which has already grown to four supercons, five permanent technical staff and about 80 users. We are now looking for a Facility Coordinator to oversee day-to-day operations. We hope to find someone with strong knowledge of NMR physics and instrumentation, who also has the ability to interact with projects in chemistry, biology etc.

NMR FACILITY COORDINATOR

UNIVERSITY NMR CENTRE

THE AUSTRALIAN NATIONAL UNIVERSITY

The University has established a research facility in high field NMR spectroscopy under the direction of Dr L.R. Brown in the Research School of Chemistry. The facility serves research projects in chemistry, biology, medicine and physics. Current equipment includes 500, 300 (wide bore) and two 200MHz spectrometers. The Facility Coordinator will be responsible for overseeing day-to-day operations of the facility, supervision of four technical staff and for consultation on NMR methodology for the research projects of staff and students. The Facility Coordinator will also have the opportunity to participate as a full collaborator in appropriate NMR research projects.

Candidates should be thoroughly familiar with advanced NMR techniques, have a sound knowledge of modern NMR spectrometers and have substantial experience with research and/or development. An appropriate degree in a relevant scientific discipline is essential and a background in computing and electronics is desirable.

Reasonable travel and removal expenses will be paid and assistance with accommodation will be provided to the successful applicant if appointed from outside Canberra. The appointee will be required to undergo a medical examination.

Written applications, quoting reference number G870566, should be forwarded to: The Secretary, The Australian National University, GPO Box 4, Canberra, ACT 2601, Australia, with whom applications close on 31 May 1987.

Candidates can get further information, including salary, selection criteria and duty statement, from me at the above address or phone numbers. Time zones and postal services being what they are, facsimile is often the surest way to communicate rapidly.

Sincerely,

L.R. Brown

L.R. Brown

Fachbereich 6
Biologie - Chemie - Geographie

Physikalische Chemie

Universität · Gesamthochschule · Duisburg

Universität -Gesamthochschule- Duisburg · Postfach 10 16 29 · D-4100 Duisburg 1

Auskunft erteilt: Prof. Dr. R. Kosfeld

Telefon (02 03)

Durchwahl 379-3319/3320

Gebäude: Lotharstraße 1, Geb. MG

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

Ihr Schreiben vom	Ihr Zeichen	Mein Zeichen	Datum
			05.03.87

(Received 17 March 1987)

Dear Barry,

this letter is to inform you that the 9th Discussion Converence of the "Fachgruppe Magnetische Resonanz" within the "Gesellschaft Deutscher Chemiker" will be held from 28.-30. September 1987 at Hünfeld (near Fulda). Main subjects are pulse methods in nuclear magnetic resonance spectroscopy. Some details you will find in the enclosed 1st circular letter. For further details please contact Dr. Pachler, whose full address is given in the bulletin.

With best greetings

Robert Kosfeld

(Prof. Dr. R. Kosfeld)

Dienstgebäude
Lotharstraße 65
(Zentralverwaltung)
4100 DUISBURG 1

Telex
855 793 uni du d

Stadtsparkasse Duisburg
Konto 200 200 400 · BLZ 350 500 00
Postgiroamt Essen
Konto 8170-437 · BLZ 360 100 43

Öffentl. Verkehrsmittel
Straßenbahn Linie 901
Bus Linie 936

GDCh

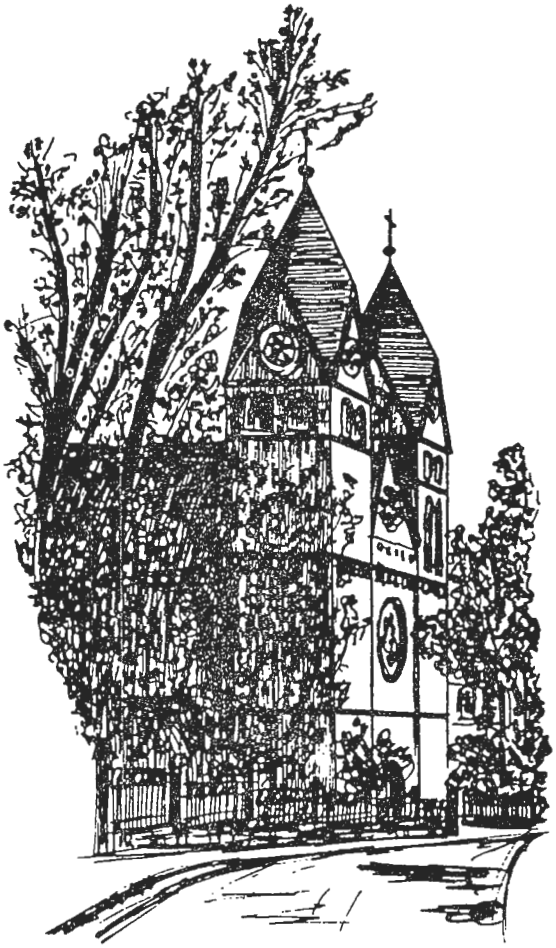
Gesellschaft Deutscher Chemiker

Fachgruppe Magnetische Resonanzspektroskopie

1. Zirkular

9. Diskussionstagung

Impulsmethoden der magnetischen Resonanzspektroskopie und Strukturaufklärung



Hünfeld (bei Fulda)
28. – 30. September 1987

Einladung

28.-30. Sept. 1987
Hünfeld

Die diesjährige Tagung der Fachgruppe Magnetische Resonanzspektroskopie vom 28.-30. September 1987 in Hünfeld soll die neuen Entwicklungen der Magnetischen Resonanzspektroskopie mit dem Schwerpunkt »Impulsmethoden der magnetischen Resonanzspektroskopie und Strukturaufklärung« behandeln.

Vorbereitung

Die Tagung wird vorbereitet von
R. Benn, R. Kosfeld, K. Pachler, H. Rüterjans

Hauptvorträge

Zu Hauptvorträgen sind eingeladen:

A. Bax, Bethesda/USA
C. Fyfe, Guelph, Ontario/Canada
H. Kessler, Frankfurt/Main
F.H. Köhler, Garching/München
G. Kothe, Stuttgart
D. Leibfritz, Bremen
K.A. McLauchlan, Oxford/UK
M. Mehring, Stuttgart
K. Möbius, Berlin
H. Peters, Ottawa/Canada
R. Scheek, Groningen/Niederlande

Unterbringung

Die Unterbringung kann weitgehend kostengünstig im Bonifatius-Kloster Hünfeld angeboten werden (100 Betten). Weitere Übernachtungsmöglichkeiten bestehen in der Stadt. Anmeldeformulare erhalten Sie mit dem Programm.

Anfragen

Anfragen richten Sie bitte an:

betreffs Wissenschaftliches Programm
Dr. K. Pachler
E. MERCK
AZL
Postfach 4119
6100 Darmstadt
Telefon (06151) 72-3348

betreffs Organisation
Gesellschaft Deutscher Chemiker
Abteilung Tagungen
Postfach 900440
6000 Frankfurt/Main 90
Telefon (069) 7917-360

Diskussionsvorträge und Poster

Sie sind herzlich eingeladen, Diskussionsvorträge bzw. Posterbeiträge **aus allen Gebieten der magnetischen Resonanzspektroskopie** anzumelden.

Vorläufige Anmeldung

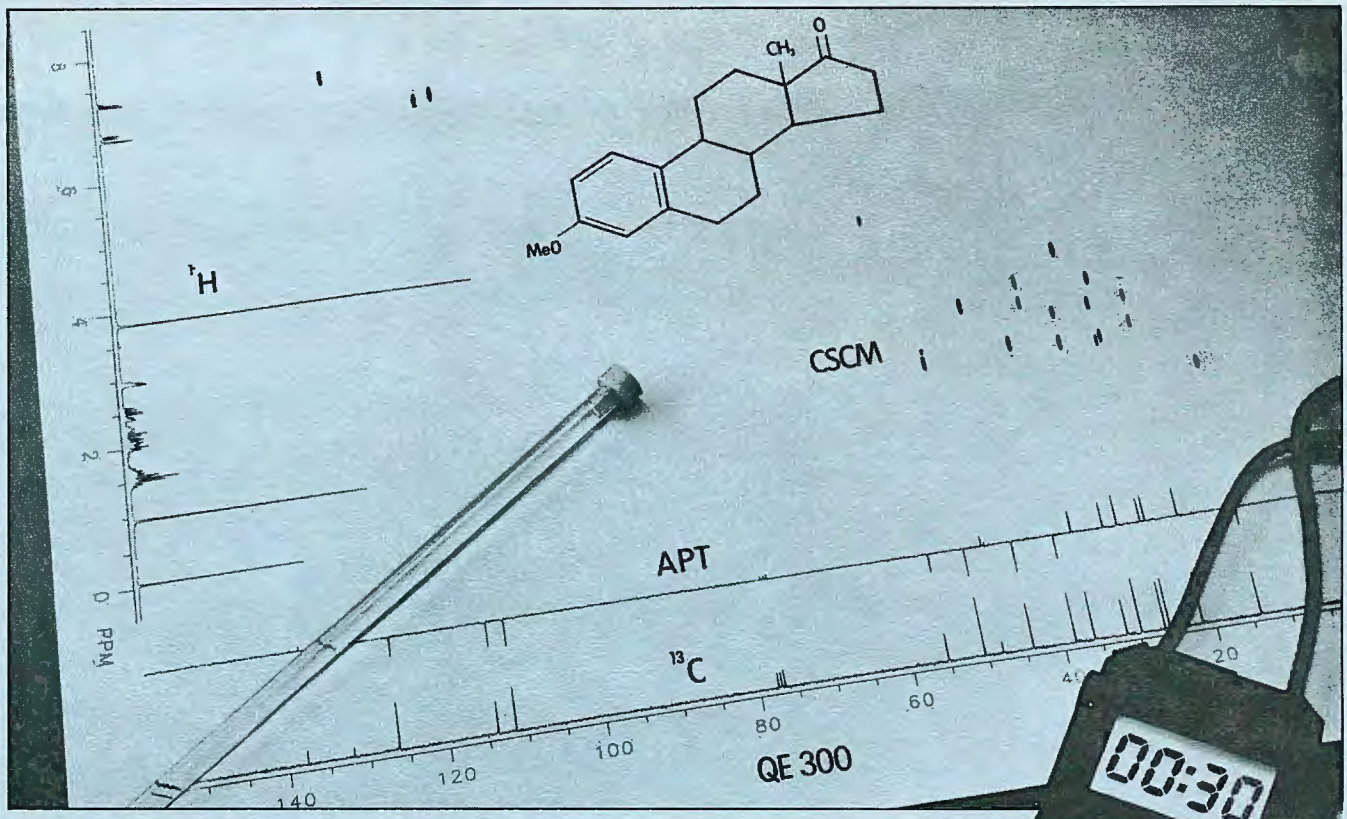
Die vorläufige Anmeldung zur Tagung sowie die Anmeldungen wissenschaftlicher Beiträge mit einer Kurzfassung des Vortrages bzw. Posters (maximal eine Seite) müssen mit den beigefügten Formblättern bis zum **30. April 1987** erfolgen an:

Dr. K. Pachler
E. MERCK
AZL
Postfach 41 19
6100 Darmstadt

Um den Tagungsteilnehmern möglichst aktuelle Zusammenfassungen von Vorträgen anbieten zu können, haben die Autoren die Möglichkeit, bis zum 15. August 1987 eine endgültige Fassung ihres Beitrages von maximal einer Schreibmaschinenseite an die oben genannte Adresse nachzureichen. Posteranmeldungen sind ebenfalls bis zu diesem Termin möglich. Die »Abstracts« werden direkt vervielfältigt und sollen deshalb das Format 25 x 16 cm nicht überschreiten.

Tagungsgebühr

Die Tagungsgebühr wird für Mitglieder DM 90,— und für Nichtmitglieder DM 150,— betragen. Studenten können kostenlos am wissenschaftlichen Programm der Tagung teilnehmen. Die endgültige Anmeldung muß bis zum 15. August 1987 erfolgen. Anmeldeunterlagen erhalten Sie mit dem Programm, das voraussichtlich im Juni 1987 versandt wird.



GE Performance!

1H, 13C, APT, and 2D NMR in ½ hour – automatically!

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

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

With the NMR industry's most advanced automation.

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

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

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

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

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

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

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

And the most complete package of hardware accessories.

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

Structural elucidation simplified.

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

High throughput and performance demonstrated.

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

GENERAL ELECTRIC

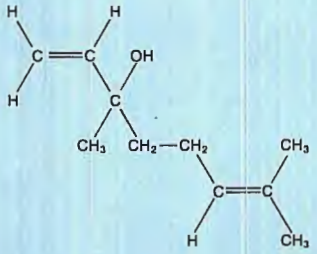
JEOL'S GX-FT NMR Systems

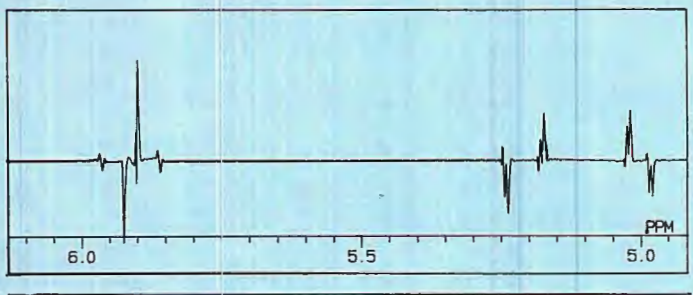
Subject: Automation

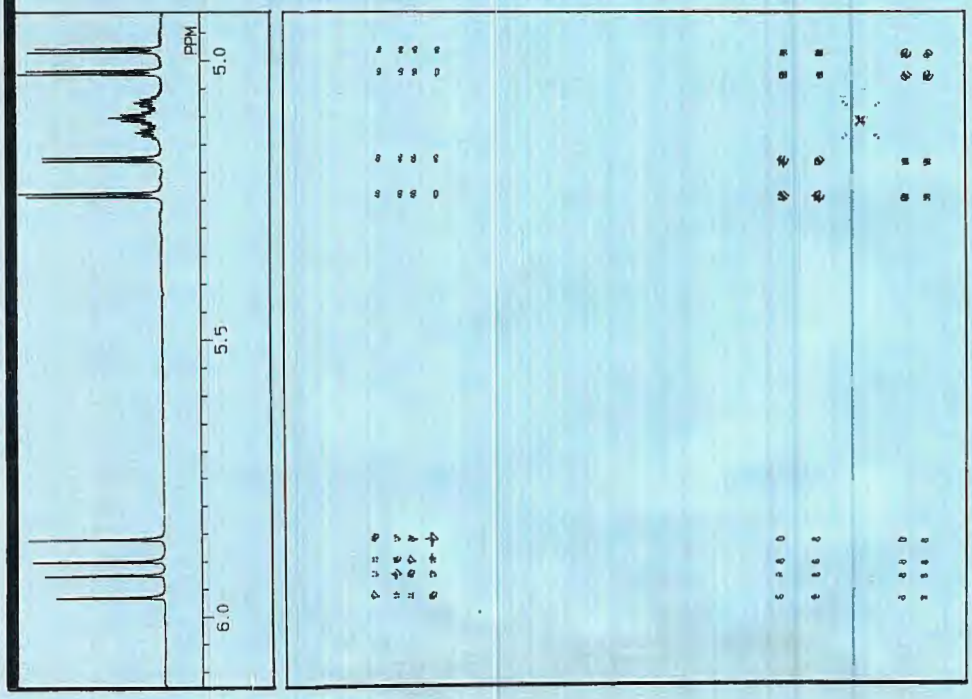
One of the more than 200 (and growing) automated routines available on the GX-Series; the data illustrates a Double Quantum Filter Phase Sensitive Cosy on the downfield section of Linalool run on a GX-270/WB (89mm) MHz spectrometer. From the moment you load the sample, spinning, lock, shimming, acquisition,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

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

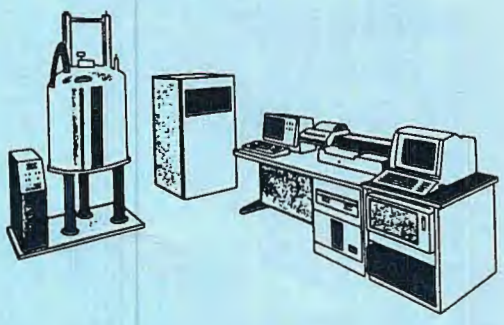
Linalool







The GX Series FT-NMR Spectrometer



For further information call:

JEOL

Serving Advanced Technology

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