P. R. Srinivasan and S.-Y. Chen
Natural Abundance Nitrogen-15 NMR Spectroscopy of Trimethylsilyl Derivatives of Secondary Amides

C. S. Yannoni

G. W. Buchanan
XL-100 System/Components for Sale

M. Barfield
Disk Drive for Sale; 2H Probe for Trade

D. E. Dorman
Computer Assisted Structure Elucidation

D. Leibfritz
Position of an NMR Spectroscopist Available

J. B. Lambert

N. K. Wilson
Substituent Parameter Analysis of 13C Chemical Shifts in Para-Terphenyls

V. Sklenar and M. Hajek
Attached Proton Test of Fossil Fuel Samples on Bruker WP-80.

R. A. Byrd
Mixing Computers in the NMR Lab and 2D H-2 and P-31 NMR in Membranes

T. Brisbane
Homebuilt 13C Insert for HFX-90's

H. A. Resing
Conductivity and Skin Depth in Anisotropic Conductors Via NMR

P. E. Ahrens
Deuterium Isotope Effects on Some Carbon-13 Chemical Shifts

A. Steigel and G. Zimmermann
Conformation of an Eight-Membered Ring System

M.J.O. Anteunis, F.A.H. Borremans and R.E.A. Callens
Relaxation Times and NOE-Factors for Pristinamycin

M. F. Roberts
500 MHz 1H-NMR Analysis of Dipalmitoyl Phosphatidylcholine Vesicle Fusion

P. A. de Jager and J. N. Breg
Reduced Sideband Intensities in 13C-NAS NMR

I. C. Belamu, C. Critchley and W. Coleman
High-Field NMR Observations on Chloroplasts and Algae

C. MacLean, F. J. J. de Kanter and T. M. Plantenga
The Electric Saturation of Molecular Alignment Studied by NMR

R. Lintvedt
Laboratory Manager - Chemical Instrumentation

B. H. Arison
Use of Lanthanides to Distinguish Meso and Racemic Forms

A. D. H. Clague
Industrial NMR Users' Meeting

G. Fraenkel
Postdoctoral Position

P. D. Ellis
113Cd NMR of Supercooled Solutions

J. L. Engle
Square to Sinewave Converter

J. F. Martin and L. S. Selwyn
A Simple Pulse Field Gradient Circuit

M. Henrichs
Two-D NMR of Solid Polymers

C. L. Khetrapal and A. C. Kunwar
What One Cannot Do, Two Can Do!

S. Brownstein
Restrictions in 2D NMR

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

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

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

Write or call for our new Catalog 781.
Dear Prof. Shapiro:

Trimethylsilyl derivatives of secondary amides have been studied by C-13 nmr spectroscopy; those of 2-pyrrolidinone (1a) and caprolactam (3a) were determined to be N-silylated (1b and 3b, respectively) while that of 2-hydroxypropyridine (4a) was determined to be O-silylated. Because of the narrow and partly overlapping C-13 chemical shift ranges reported for lactam carbonyls (173-180 ppm) and imino carbons (167-179 ppm) ample room for ambiguities exists. We therefore felt that nitrogen-15 nmr spectroscopic study of the above-mentioned derivatives would provide unambiguous evidence for their structures in view of the large difference in the N-15 chemical shift ranges reported for amide (110-120 ppm for \( \gamma, \delta, \varepsilon \ldots \) lactams, 95-140 ppm for other saturated amides) and imino nitrogens (280-380 ppm). In addition to the above three TMS derivatives, shifts for the TMS and N-methyl derivatives of 2-piperidinone (2a) were measured. It is clear from the observed N-15 chemical shifts (indicated against each compound) that the TMS derivatives of 2-pyrrolidinone, 2-piperidinone and caprolactam are N-silylated and that of 2-hydroxypropyridine is O-silylated. Witanowski et al \(^3\) had reported that N-14 nmr studies of 2-hydroxypropyridine showed it to exist mostly in the 2-pyridone form; our measurements in dimethylsulfoxide and water confirm their results. They also "calculated" the nitrogen shift for the hydroxy form 4a to be 89.0 ppm deshielded from that of 2-pyridone (4d); this value (at 260.5 ppm) lies at the most shielded range for pyridine derivatives\(^2\).

contd...
1: a, R=H (114.7)  
b, R=SiMe₃(116.6)  
c, R=CH₃(109.5)  

2: a, R=H (114.3)  
b, R=SiMe₃(115.7)  
c, R=CH₃(108.7)  

3: a, R=H (117.6)  
b, R=SiMe₃(120.7)  

c, R=CH₃(120.7)  

4: a, R=H (260.5)  
b, R=SiMe₃(278.9)  
c, R=CH₃(268.1)  

d, R=H (171.5)  
e, R=CH₃(169.1)  

(all N-15 shifts are in ppm w.r.t. anhydrous liquid ammonia)

Sincerely yours,

Puliyur R. Srinivasan  Shiange-Yun Chen

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

Dear Barry,

The next ENC will be held at the Concourse Hotel and Convention Center in Madison, Wisconsin, April 25-29, 1982. The meeting will have a minimum number of formal sessions, opening up more time for individual discussion. Tentative plans include sessions on solids, 2-D and multiple quantum spectroscopy, quadrupolar nuclei, sensitivity enhancement/selective excitation, and a potpourri of special techniques. There will be poster presentations, and we hope to keep posters up (space permitting) throughout the meeting. Anyone interested in presenting a poster should contact the poster session Chairman, Dr. David Lankin, Borg-Warner Corporation Research Center, Wolf and Algonquin Roads, Des Plaines, IL 60018, before January 15, 1982. We encourage the presentation of novel experimental methods.

Registration information and a preliminary program will be sent in January to those on a mailing list consisting of attendees at the last five ENC's, so anyone who thinks he/she is not on this list should contact the ENC Secretary, R. G. Bryant.

Local arrangements are being handled by T. C. Farrar.

Sincerely yours,

C. S. Yannoni  
Chair, 23rd ENC  
IBM Research Laboratory  
Dept. K34/281  
5600 Cottle Road  
San Jose, CA 95193
The GX-400 represents a totally new design concept, based on years of JEOL technical experience. It's not an NMR that uses a computer or a computer that uses an NMR. But, a completely integrated spectrometer that employs a 400 MHz Solenoid which, of course, provides outstanding sensitivity, resolution and dispersion.

Great. Of course. But that's only part of the whole concept that makes the JEOL GX-400 an exceptional NMR system. **There's the SIC diagnostics (Status Integrity Check), for instance, that will self-monitor the spectrometer hardware and functions** • computer/rl. fiber optics link • comprehensive pulse programming • auto-lock & auto-tune • JEC-32 long word mini-computer (32 bit word) • up to 256K word memory • 12 inch raster scanner display with graphics package • light pen control system and/or keyboard • 150 character-per-second printer • comprehensive magnetic media and more, much more.

And, if all this isn’t enough to convince you of how serious we are about providing the best NMR available... here's more. We built in flexibility through an LSI based MPU that provides total and complete spectrometer control and allows state-of-the-art expandability so you'll never outgrow the GX-400. And, incidentally, all of the great capabilities of the GX-400 are also available from JEOL in the GX-500 (500 MHz) model.

You might ask more from a great NMR and there is more. To find out how much more, call or write...
Dear Barry:

We have just received notice of funding for a superconducting NMR, and offer our present XL-100-12, equipped with the NTC F.T. accessory, for sale.

It should be noted that the magnet is the narrow gap 12 variety. Probes available are 5 mm $^1H$ (V.T.), 5 mm $^{13}C$ (V.T.) and 8 mm $^{13}C$ (Room Temp). The computer is the Nicolet 1080 (16K), equipped with Nicolet 293 pulse controller as well as a Diablo Disc and NIC 294 unit.

Anyone interested in purchasing the complete system or specific parts should contact me as soon as possible.

Sincerely,

G.W. Buchanan,
Associate Professor.

phone (613)-231-2723

THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA 85721

COLLEGE OF LIBERAL ARTS
DEPARTMENT OF CHEMISTRY

Disk Drive for Sale; $^2H$ Probe for Trade

Dear Barry:

With all of the wheeling and dealing in used equipment, you may have to set-up an auxiliary newsletter to handle the volume. This is our contribution to Smiling Barry's Used NMR Lot.

With the recent addition of an Aspect 2000A/real time clock/CDC disk drive to our WM-250 FT NMR, we have available for sale a 12 megabyte Diablo Model 448 dual disk drive. This was working fine when we pulled the plug several weeks ago, and we have several cartridges and filters, which will be included.

Since all of our deuterium NMR is now being carried out on the WM-250, we would like to trade our $^2H$ observe channel (probe, preamp, and pulser unit with external $^2H$ lock) for the WH-90 for some other probe, such as $^{11}B$, $^{31}P$, or whatever.

Sincerely yours,

Mike Barfield
602-626-3465
Professor B. L. Shapiro  
Department of Chemistry  
College of Science  
Texas A and M University  
College Station, Texas 77843

Dear Barry:

COMPUTER ASSISTED STRUCTURE ELUCIDATION

From a recent item in C and E News (April 13, pp. 29-30) it was obvious that some of our colleagues who seek to develop computer-assisted methods for interpretation of spectroscopic data have become somewhat discouraged. This I hate to see; perhaps those of us who have made successful use of these programs have been lax in reporting these successes. I should like to report briefly some of our experiences with these methods. Readers will, I hope, understand the necessity of omitting many of the interesting details.

One of the many tasks performed by my colleague, Jon Paschal, is the early spectroscopic examination of "new isolates." We now routinely use the NIH/EPA CIS system to check that these isolates are indeed new. I regret to report that some are not. In one case, the only reliable data we had deduced was the empirical formula (peak matching in the mass spectrometer) and the presence of a C-methyl group (1H NMR). With these inputs the SANSS component of CIS gave us a list of five possibilities, and the first one printed was found to be correct. It does not seem to be widely known that the CIS system includes, among other things, the 9th Edition of the Merck Index in substructure-searchable form.

Of course, the CIS system also includes a 13C data base, and I have spent many hours (and dollars) exploring its potential. We are trying to determine whether various types of functional groups can be associated with specific combinations of resonance positions. Unfortunately, there are many unassigned and incorrectly assigned resonances in the data base, and this has made our progress toward our goals rather slow.
We have also had a lot of experience with the DENDRAL programs from Stanford University. We have advanced from CONGEN to GENOA, and have had at least one remarkable success. In this case, an example of an unexpected product from a reaction with a known starting material, GENOA eventually proposed four final structures. These structures were complete surprises, and I simply did not believe them when the computer drew them. It took another day's work before I recognized that a rearrangement had led to a very unexpected structure. We selected one of the four structures as being the most likely, and our choice was later confirmed by crystallographic studies. I hope that we can some day tell a more complete story about this one.

At the moment we are deeply involved in exploring the potential of the method of \(^{13}C\) data base construction and use developed by the DENDRAL group (e.g., N.A.B. Gray et al., J. Org. Chem., 46, 703). This is the first system which allows us to build our own \(^{13}C\) chemical shift/molecular structure data base. As yet, we have not used it in any "real-life" situations, but we are quite excited by our results from some initial "contrived" tests using anthraquinones. The program is still very experimental and can be used only on the Stanford computer, but my own opinion is that this approach is the best available for many of the applications problems in labs like ours.

Yours sincerely,

Douglas E. Dorman, Ph.D.
Research Scientist
Physical Chemistry Research

---

Position of a NMR spectroscopist available

In our department the position of a NMR spectroscopist is vacant. It is a permanent position. The cross income amounts DM 45 000 - 52 000 p.a. The applicant must have a doctoral degree in physics or chemistry. Some experience with 2D-FT is preferred. Currently we use a Bruker WH 360 and a 60 MHz instrument. One further spectrometer is planned. The application should include two references.

Yours sincerely,

( Prof. Dr. D. Leibfritz )
A NATO Advanced Study Institute on the subject of "The Multinuclear Approach to Magnetic Resonance" will take place in Stirling, Scotland, August 23 to September 3, 1982. The two week Institute will have lectures on NMR applications of all nuclei except $^{1}H$, $^{13}C$, and $^{31}P$. Additional lectures will be concerned with instrumentation, relaxation times, chemical shift calculations, 2D and CP methods, solid state methods, and dynamic processes. Several multinuclear instruments will be present for the hands-on training and use of the participants. All areas of chemistry will be included. The tentative list of lecturers includes: C. Brevard, P. D. Ellis, J. A. Elvidge, S. Forsén, R. Freeman, R. K. Harris, R. G. Kidd, W. G. Klemperer, J. B. Lambert, P. Laszlo, R. L. Lichter, O. Lutz, K. J. Packer, J. Reisse, I. C. P. Smith, and G. A. Webb. Further information may be obtained from the Directors:

Professor Joseph B. Lambert  
Department of Chemistry  
Northwestern University  
Evanston, Illinois 60201 U.S.A.

Dr. F. G. Riddell  
University of Stirling  
Stirling FK9 4LA  
SCOTLAND

Sincerely,

Joseph B. Lambert

JBL:sm
Never before in the history of NMR has time so optimally been shared between processes. Bruker's DISNMR, the first true time-sharing NMR data system allows you to process several data sets simultaneously. For example: you may perform more than one Fourier transformation while executing a PASCAL program at the same time. With the virtual memory capability of DISNMR and multi-tasking architecture acquisition of data never interferes with any I/O devices or whatever jobs are performed by the system. It permits disc acquisition and transformation of up to 256K data tables. This is illustrated by the ultrahigh-resolution 600 MHz spectrum showing the expanded ethylbenzene methylene quartet at 2.65 ppm, obtained by disc acquisition of a 128K FID and subsequent transformation of 256K data points, revealing a stunning amount of fine structure.

DISNMR does not require new hardware; it is fully compatible with all ASPECT data systems. The new DISNMR puts Bruker's WM series of spectrometers in a class by itself.

For complete facts simply write "DISNMR" on your stationery and mail it to Bruker Instruments, Inc., Manning Park, Billerica, MA 01821.

In high-field NMR there is simply no alternative.
For information on NMR and EPR instrumentation and accessories your prime source is the nearest Bruker office:

Bruker Instruments, Inc.
Manning Park, Billerica, MA 01821
(617) 667-9580

201 San Antonio Circle, Suite 152
Mountain View, CA 94040
(415) 941-3804

539 Beall Ave., Rockville, MD 20850
(301) 762-4440

1603 Darwin Court, Wheaton, IL 60187
(312) 668-4441

Call or mail this coupon to the nearest Bruker office.

Please send me more information on the new DISNMR

The information is needed for future planning □ for purchase after 6 months □ for immediate purchase □ Please have your specialist contact me □

My telephone number is: ( ) ____________________________

I am also interested in NMR systems □ My field of application is: ________________________________

Name: ____________________________________________

Institute/Company: __________________________________

Address: __________________________________________

City/State/Zip: ______________________________________
Dear Barry:

Polychlorinated terphenyls (PCTs) have recently been identified as ubiquitous contaminants in human tissues. As part of a program to characterize spectroscopically various terphenyl isomers, Dan Zehr and I have measured substituent effects on the $^{13}$C NMR chemical shifts of several 4-substituted $p$-terphenyls, below.

The $\Delta \delta$ values were correlated with various Hammett $\sigma$ parameters, employing single-parameter, $\Delta \delta = \rho \sigma$, dual-substituent-parameter (DSP), $\Delta \delta = \rho_1 \sigma_1 + \rho_2 \sigma_2$, and dual-substituent-parameter-with-non-linear-regression (DSP-NLR), $\Delta \delta = \rho_{1R} \sigma_{1R} + \rho_{2R} \sigma_{2R}/(1 - \varepsilon \sigma_R)$, relationships. No acceptable correlations were obtained for C-3$^{15}$ and C-4. A single parameter $\sigma_{3R}$ was adequate at only two positions, C-2',6' and C-2$^{11}$,6$^{11}$. At positions C-1; C-2,6; C-3',5'; C-1'; C-3$,5$'; and C-4' the DSP model and $\sigma_R$ were best. At para-type positions in the central ring, C-1' and C-4', the DSP-NLR model was best. The ratio $\lambda = \rho_2/\rho_1$ of mesomeric to inductive transmission of electronic substituent effects ranged from 0.535 to 4.58, indicating the importance of inductive electronic effects at nearly all positions in $p$-terphenyl, even at C-4', the carbon farthest from the substituent, where $\lambda = 1.70$.

Details are given in a manuscript we have recently submitted for publication.

With best wishes,

Sincerely,

Nancy K. Wiston, Chief
Chemical Characterization Section
Analytical Chemistry Branch (MD-69)
Attached Proton Test of Fossil Fuel Samples on Bruker WP-80

Dear Professor Shapiro:

Before the mailing of our third contribution to TAMUNMRN concerning the use of the pulse sequence published by Le Coq and Lallemand (1), we received TAMUNMRN No. 273, where Schoolery and Patt explained the use of this technique. They named their similar pulse sequence "Attached Proton Test" (APT). We like this name and we think the abbreviation APT is suitable for the group of experiments which are able to distinguish various carbon atoms. Hence we abridged our letter and Figures 1 and 2 show the use of APT method (1) in the field of $^{13}$C NMR spectroscopy of fossil fuels. Figure 1 shows broad band decoupled, SFORD and APT spectra of the crude oil (Forties). The separation of $\text{CH}_2\text{C}$ and $\text{CH}_3$ groups is evident from APT spectrum.

---

Figure 1 - crude oil
a) broad band decoupled spectrum
b) SFORD spectrum
c) APT spectrum
In the aromatic part of the spectrum of the coal pitch oil - Fig. 2 the APT spectrum gives possibility to distinguish aromatic quarternary (C_q) and CH carbon atoms.

Pulse program for WP-80:

<table>
<thead>
<tr>
<th>PW1</th>
<th>PW2</th>
<th>PW3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8μs</td>
<td>16μs</td>
</tr>
</tbody>
</table>

We measured both above mentioned samples on Bruker WP-80 spectrometer and parameters of the measurement are described in figures. It seems us that APT experiments will be useful in 13C NMR analysis of mixtures, where SPORD spectra bring little information.

With best regards

Vladimir Sklenar
Institute Sci. Instrument
Brno

Milan Hajek
Prague Institute of Chem. Technology

Mixing Computers in the NMR Lab and 2D H-2 and P-31 NMR in Membranes

Many TAMU readers will recall the discussion concerning computer systems at the recent ENC. Whether people agree on a particular method of having distributed processing computer systems connected to their nmr equipment or not, the inevitability of this situation is clear. In this regard, I would like to offer our experiences at NRC as an example of how beneficial a move this can be.

At the time of the ENC, we had already been through the design phase of the system and had begun discussions with the manufacturers. We had chosen to go the route of commercial nmr computers rather than a system with general purpose computers, like that described by David Reuben. The reasons for this decision were many, and rather than dwell on this topic, I would like to describe just the implementation of our decision. The system which we put together is shown schematically in figure 1. Note that our NMR equipment consists of a Bruker CXP-300 and a home-made solids spectrometer which has been dubbed the PHOENIX-200; it has been the subject of previous contributions to TAMU.

The equipment purchased to set up our distributed processing system consisted of the data station computer and a data acquisition computer, including a pulse programmer to facilitate interfacing to the PHOENIX-200. We chose Nicolet equipment for our system. At first glance this may appear foolish, since we would then be faced with the problem of interfacing a Bruker ASPECT computer with the Nicolet 1280. However, this has been easily accomplished with rather small software modifications; there were NO hardware changes made to either computer system. For our system we wished only to transfer data collected on the CXP-300 to the Nicolet-1280 data station. This was readily accomplished using the second RS-232C channel of the ASPECT.
To control the data transfer, we combined the Bruker utility program BICON with a modified version of CXP software. Then by replacing a few commands in the CXP program, we were able to transmit data blocks out on the RS-232C line. The format is signed decimal integers. Some further modifications were made to the CXP software to permit these transfers to include pertinent spectrometer parameters associated with the data file and to be made in an automation sequence, hence we are able to transfer entire blocks of data from the disk of the ASPECT to the 1280. The receiving program on the Nicolet-1280 accepts the data file and writes it onto the disk using the same name (truncated to 6 char.) as was used for the ASPECT file. This program also shuffles the data from a mixed format (R,I) to an array format, compatible with the Nicolet system. Files created by the receiving program are then processed by the standard Nicolet software. The final feature of the software is the ability to perform the proper format conversion for files of a 20 data set collected on the CXP. This conversion is done "on the fly", such that the data exist as a collection of files on the ASPECT disk (without the need to be stored sequentially) and after the transfer exist as a proper .DAT file on the Nicolet disk ready for processing.

Transfer of data between the PHOENIX-200 and the data station is performed with standard software available from Nicolet. All data transfers indicated in figure 1 are done at a rate of 19.2 kBAUD. Transfer of an 8k file takes approximately 30 seconds.

As an example of the power of such a system, we show in figures 2 and 3 some two-dimensional spectra for which the data was collected on the CXP-300 and processed on the Nicolet-1280 data station. All of the time consuming processing and plotting of this data is done completely off-line from the spectrometer, freeing it to do more data collection. Furthermore, these spectra represent the justification for the system which we chose. While recent software updates from Bruker have permitted us to process CXP two-dimensional data, these software packages greatly restrict the types of processing which can be done; whereas, the Nicolet software package is general enough to allow us the needed flexibility in our 2D data processing. As a result, this combination of Bruker and Nicolet equipment, although somewhat unorthodox, permits us to pursue some exciting new areas of solid state 2D NMR in membranes. The experiments shown in fig. 2 and 3 illustrate some of our recent results in this area. The presentation shows the normal frequency (1D) spectrum in one dimension and the linewidth in the second dimension. Due to built-in processing features of the Bruker 20 package, this proper lineshape representation cannot be obtained by processing the data with Bruker software. These experiments resulted from some very stimulating discussions with Dr. Mark Henrichs of Kodak. Further work is in progress to exploit the power of our distributed processing system and the two solid state spectrometers.
I might add that the entire installation of the system, including software development by myself and Mark Rance (a postdoctoral fellow in our lab) and interfacing a Nicolet 293B to the Phoenix-200 took approximately 6 weeks, during which operation of the CXP was uninterrupted. We received substantial assistance from both Bruker, in regards to the BICON program, and Nicolet, in regards to some initial programming of the receiving software, for which we are very grateful. Although there are some forthcoming components to our system, we feel we are off to a good start!

Please credit this contribution to the NRC account in Dr. Ian Smith's name.

Sincerely yours,

R. Andrew Byrd

RAB: jm

**Figure 1**

![Diagram showing the CXP-300 Spectrometer, Phoenix-200 Spectrometer, Nicolet 1280 (64K), and related components.](image)
Fig. 2. 46.06 MHz $^1$H 2D NMR spectrum of an egg lecithin dispersion in water containing 13 mg of 4,4-d$_2$ oleic acid. The usual quadrupolar powder pattern is easily seen in the first dimension. The second dimension reveals the linewidth of isochromats with different orientation with respect to the field. Total data matrix $32 \times 512$, total experiment time $\sim 17$ hrs.

Fig. 3. 121.47 MHz $^{31}$P 2D NMR spectrum of the same sample as Fig 2. In this example, the normal CSA powder pattern is seen in the first dimension, and the linewidth is again seen in the second dimension. Total data matrix $64 \times 512$, total experiment time $\sim 10$ hrs.
September 2, 1981

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

Title: Homebuilt $^{13}$C Insert for HFX-90's.

Dear Dr. Shapiro,

We routinely achieve a s/n ratio for $^{13}$C (10 mm tube of 90% ethyl benzene) of ~100:1. Our goal was to improve on this performance by increasing the filling factor of both the receiver and decoupler coils.

The new receiver coil (single #32 AWG copper wire) was wound on a machined piece of paraffin wax threaded for the correct number of turns and spacing which were determined experimentally. This was inserted into a piece of precision tubing (i.d. = 11 mm, o.d. = 12 mm) and the coil glued in place with Aron Alpha, a quick setting adhesive. The paraffin wax was removed by placing the assemblage in hot water. The $^1$H decoupler coil was mounted on the inside of a standard Bruker dewar. New pieces of deiron spacers were necessary to accommodate the new insert.

Tests on the completed insert gave a respectable 40-45% improvement in signal/noise. Fig. 1 is a standard spectrum obtained with a Bruker insert giving ~108:1. Fig. 2 is our homebuilt insert giving ~155:1. The coil has an inductance of 1.5 µH and a self resonate frequency of 76 MHz; these values closely match those of the standard insert. The $^1$H lock level is somewhat larger on the new insert.

Further tests are planned on a $^3$P insert as well as experimentations with smaller o.d. dewars constructed in our glass shop. This may alleviate the tedious mounting of the decoupler coils on the inside of the dewars.

Please credit this contribution to Dr. Tom Nakashima's account.

Sincerely,

Tom Brisbane

TB/ss
Dear Professor B. L. Shapiro:

"Conductivity and Skin Depth In Anisotropic Conductors Via NMR"

Intercalation of AsF$_5$ into highly oriented pyrolytic graphite (HOPG) produces a material which is a highly anisotropic, two-dimensional electrical conductor. We have been able to show experimentally that an oscillating magnetic field, $B_1$, can penetrate two-dimensional conductors uniformly when the axis of poor conductivity is perpendicular to the axis of polarization of $B_1$. In this orientation, eddy currents are negligible, the interior of the body is not shielded, and the NMR experiment detects all the nuclear spins in the body. If the axis of poor conductivity is parallel to $B_1$, eddy currents are induced in the plane of easy conductivity and NMR detects only those nuclei within the skin depth. From these two experiments, it is possible to estimate the conductivity in the plane of easy conductivity.

An important result is that it is not necessary to pulverize the sample to reduce the dimensions of the crystal to less than the skin depth. Indeed, the signal strength is maximized by orienting $B_1$ perpendicular to $B_1$.

These ideas are illustrated in the accompanying figures. For the AsF$_5$ intercalated graphite used in these experiments, a skin depth of ~12 µm and an in-plane conductivity of ~2.7 x 10$^5$ ohm$^{-1}$ cm$^{-1}$ were determined. The work is described in a paper recently submitted to J. Chem. Phys. (H. A. Resing, M. J. Moraéz, and G. R. Miller, "AsF$_5$ Intercalated Graphite: Conductivity and the Anisotropy of the Skin Depth Via NMR Spectroscopy").

Please keep TAMU Newsletter coming to NRL in care of Bill Moniz. Thank you.

Sincerely,

Henry A. Resing
Polymeric Materials Branch
Chemistry Division
Fig 1. $^{19}$F NMR spectra for AsF$_5$ intercalated to first stage in highly oriented pyrolytic graphite. a) no eddy currents b) eddy currents.

Fig 2. Representation of an anisotropic conductor in an oscillating magnetic field; $\delta$ is the skin depth.
Dear Prof. Shapiro

Since I left Aarhus, I have been missing TAMU letters. I therefore hope that you will accept the following contribution as a first installment of the subscription fee.

In Roskilde Fritz Duus and I have been investigating deuterium isotope effects on $^{13}$C chemical shifts in some $\beta$-thiooxoketones and Schiff's bases of salicylaldehyde.

![Chemical structures](image)

The isotope effects are defined in the following way:

$$\Delta = \delta^{(H)} - \delta^{(D)}$$

where $n$ is the number of bonds separating the carbon in question and the deuterium.

Some unusually large isotope effects over two bonds are observed. Notice the negative sign and notice also the long range isotope effects of both signs.

**Data in ppm**

![Chemical structures](image)
These unusual isotope effects are not caused by normal deuterium isotope effects as these usually are small and short range.

The reason for the large effects is a change in the tautomeric equilibrium position upon deuterium substitution. The magnitude of the effects depend e.g. on

$$\Delta 'CS' = \delta CS - \delta CSH \sim 90 \text{ ppm}$$

The method is hence very sensitive and may report even very small changes in the equilibrium constant and is thus very sensitive as a tool to establish the presence of a tautomeric equilibrium.

We have also looked at Schiff's bases, but in this case are the effects much smaller.

Reprint requests

All papers (reprints or preprints) dealing with isotope effects on chemical shifts are warmly welcome as I in the near future are going to write a review on this subject to appear in Ann.Reports on NMR.

Comments on the best way of defining the isotope effect will also be appreciated.

Yours sincerely

Poul Erik Hansen
Conformation of an eight-membered ring system

Dear Professor Shapiro:

In the course of NMR studies on benzolactams we observed unusual high barriers to ring inversion in the 3, 4, 5, 6-tetrahydro-1-benzazocin-2(1H)-one system. The free enthalpy of activation of the N-methyl derivative, estimated from the coalescence of the resonances of the benzylic protons 1 and 2, amounts to ca. 89 kJ/mol (21.3 kcal/mol).

Since the 270 MHz 1H NMR spectrum of this compound is well resolved in the spectral region of the tetramethylene chain at ambient temperature, we attempted an analysis of the 8-spin system using the PANIC program.

Although perfect agreement of the experimental Lorentzian-to-Gaussian resolution enhanced spectrum (Fig. a) and calculated spectrum (Fig. b) has not yet been achieved, it may be worthwhile to comment on the present stage of simulation.

The large vicinal coupling constants $^3J = 12.4 - 12.8$ Hz between the pseudoaxial protons 2, 8, 7, and 5 clearly prove the exclusive presence of the twist-boat-chair conformation. Difficulties are met however in the assignment of the long range couplings occurring in the tetramethylene chain, to the benzene nucleus, and perhaps to the N-methyl group, primarily accounting for the lack of perfect agreement in the present simulation. One of these, $^4J_{1,6} = 0.75$ Hz, already has been included in the calculation (Fig. b); $^4J_{3,4}$ not yet.

Surprisingly, it appears that in contrast to the pseudoequatorial benzylic proton 1 its pseudoaxial counterpart 2 is not involved in appreciable long range couplings to the aromatic protons. Any comments on this behavior are welcome.

Sincerely yours,

Alois Steigel
Univ. Düsseldorf

Gottfried Zimmermann
Univ. Frankfurt
Dear Barry,

We have recently been determining the $^{13}$C-$T_1$ relaxation times and the $^{13}$C-$^1$H-NOE-factors of pristinamycin IA, a cyclic depsipeptide antibiotic (fig.) on our WP-200 Bruker instrument. We used the saturation recovery technique together with the three parameter treatment of the experimental data (cfr. eq. 1).

$$S_t = S_0 [1 - C \exp (-t/T_1)]$$  \hspace{1cm} (1)

During our dynamic NOE-measurements we also obtained a series of $T_1$ values which were in good agreement with the other one's (the dynamic NOE factors were elaborated using eq. 2).

$$S_t = S_0 [\eta + \eta \exp (-t/T_1)]$$  \hspace{1cm} (2)

Also the accordance between statically and dynamically determined NOE-factors was satisfactory. Interpretation of the data (Table I) was rather straightforward. Given the identical $T_1$'s for all ring-$\text{CH}$-carbons the molecule must tumble isotropically. The $\gamma$-oxo Pip, the $\text{NMe}_2$, $\text{Me}$ and the $\text{OH}$-Pic residues have $T_1$ values identical to the depsicycle backbone. The PhGly residue has an extra mobility about its $\beta$-$\alpha$ axis, the D-Abu side chain shows segmental motion while the trans-linked Pro residue shows enhanced $T_1$-values for its ring carbons. All these data find an explanation using our earlier proposed model of these antibiotics. (1). Full details can be found in a forthcoming paper.

### TABLE I

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>T&lt;sub&gt;1&lt;/sub&gt;</th>
<th>N&lt;sub&gt;e&lt;/sub&gt;</th>
<th>α</th>
<th>μ</th>
<th>T&lt;sub&gt;2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thr</td>
<td>s</td>
<td>56.34</td>
<td>1</td>
<td>0.38</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>71.96</td>
<td>0.36</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ</td>
<td>76.81</td>
<td>0.74</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-OM Pid</td>
<td>γ</td>
<td>127.12</td>
<td>1</td>
<td>0.40</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>129.27</td>
<td>0.39</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>140.04</td>
<td>0.45</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abu</td>
<td>s</td>
<td>51.59</td>
<td>1</td>
<td>0.39</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>51.81</td>
<td>0.74</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ</td>
<td>10.00</td>
<td>1.05</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prol</td>
<td>s</td>
<td>57.67</td>
<td>1</td>
<td>0.39</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>27.86</td>
<td>0.38</td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ</td>
<td>24.72</td>
<td>0.50</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>47.93</td>
<td>0.25</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pMe&lt;sub&gt;2&lt;/sub&gt;Phe</td>
<td>s</td>
<td>54.26</td>
<td>1</td>
<td>0.38</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>35.87</td>
<td>0.22</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>130.62</td>
<td>0.39</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>112.95</td>
<td>0.39</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMe&lt;sub&gt;3&lt;/sub&gt;</td>
<td>31.11</td>
<td>1.3</td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>40.68</td>
<td>2.3</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>h-oxo-Pip</td>
<td>s</td>
<td>57.09</td>
<td>1</td>
<td>0.35</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>41.46</td>
<td>0.21</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>39.15</td>
<td>0.22</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>37.05</td>
<td>0.20</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phgly</td>
<td>s</td>
<td>34.16</td>
<td>1</td>
<td>0.39</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>127.61</td>
<td>1.0</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>128.98</td>
<td>1.0</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>128.28</td>
<td>0.42</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) For explanation of carbon codings see Figure.
b) N is the number of directly attached protons.
c) Errors on T<sub>1</sub> values are estimated to 3-10%.
d) Mean value of static and dynamic measurements; errors are estimated to 15-20%.
e) Assignment might be reversed.
Lacking ready access to light-scattering or EM apparatus and disliking the
tedium of sizing columns, we have yet another way to analyze the size of
dipalmitoyl-phosphatidylcholine (DPPC) sonicated vesicles based on their
$^1{H}$-NMR spectrum at very high fields. At 6.3T or higher, the DPPC choline methyl group
is split into two peaks which represent the very slowly exchanging inner and outer
phospholipid monolayers. At 11.7T (500 MHz) this splitting is quite clear and
varies above (Fig. 1B) and below (Fig 1A) the phase transition temperature
($T_c = 37^\circ C$). Similar chemical shift differences between inner and outer
phospholipids above (0.036ppm) and below (0.073ppm) $T_c$ have been documented
by Eisenberg and Chan$^1$ for distearoyl phosphatidylcholine vesicles. If small
unilamellar DPPC vesicles (250Å) are incubated below $T_c$ for various lengths of time
fusion will occur.$^2$ This can be detected in the $^1{H}$-NMR spectrum above $T_c$ by a new
splitting of the inner choline methyl peak. The new peak (or shoulder) is
intermediate between the outer choline peak and the original and still observable
inner choline peak (Fig. 1C). This is seen best in a convolution difference
spectrum of that region (Fig. 1D). In a spectrum taken below $T_c$ increased line­
widths make it difficult to discern multiplicity of the inner peak. As more and
more vesicles fuse the new "inner" peak grows in relative amplitude. The discrete
doubling of the inner methyl peak suggests a bimodal distribution of vesicle sizes.
This agrees with EM and gel filtration studies where 230Å and 600Å vesicles
predominate under similar fusion conditions. In fact, the chemical shift
difference of inner and outer choline methyl peaks can be calibrated with sized
vesicles and used to estimate the diameter of other preparations.

Sincerely,

Mary F. Roberts

2 D. Lichtenberg, E. Freire, C.F. Schmidt, Y. Barenholz, P.L. Felgner, and

MFR/meb
Fig. 1: Choline methyl region in DPPC sonicated vesicles;
0 denotes outer monolayer resonance,
I denotes the inner layer methyl resonance at
(A) 28°C;
(B) 41°C;
(C) 41°C after fusion has occurred (I₁ corresponds to the
normal inner choline peak, while I₂ only appears upon fusion);
(D) convolution difference spectrum of (C) showing the two inner
choline peaks.
Dear Prof. Shapiro,

Some months ago we started $^{13}$C-MAS NMR experiments on large biological systems with our new Bruker CXP 300. Spectra of these systems are generally crowded with resonances in which sideband contributions are difficult to assign.

Recently, W.T. Dixon proposed a complicated pulse sequence to get spinning sideband free spectra (J. Magn. Res. 44 (1981) 220). This method uses four $180^\circ$ pulses with different delays and the acquisition starts after two sample revolutions. We have experimented with an alternative method using one $180^\circ$ pulse after one half revolution. The acquisition starts after one revolution (figure 1). This results in a spectrum with inverted sidebands. A summation of this spectrum and a normal spectrum (figure 2) gives a cancellation of first-order sidebands (figure 3).

When the chemical shift anisotropy is relatively high compared to the spinning frequency, second-order sidebands can not be neglected. In this case our method does not eliminate these second-order sidebands and in addition the intensity of the centre-band is reduced.

Please credit this contribution to prof.dr. T.J. Schaafsma.

Sincerely,

P.A. de Jager

Agricultural University/Transitorium, De Dreijen 11/6703 BC Wageningen/The Netherlands/Tel. (08370) 82044/82634
Glycine in Delrin rotor
MAS frequency 5kHz

Figure 1

Figure 2

Figure 3
September 1, 1981

HIGH-FIELD NMR OBSERVATIONS ON CHLOROPLASTS AND ALGAE

Dear Professor Shapiro:

We received recently your orange slip and the following is our reply to your ultimatum.

This is a preliminary report of high-field proton and $^{35}$Cl NMR spectra of chloroplasts and partially deuterated algae. We are observing such spectra as a means of studying the oxygen evolving mechanism (photosystem II) of photosynthesis.

In the case of 'intact' (Class A) or 'broken' (Class C) spinach chloroplasts prepared in 0.4M sorbitol buffers, the proton magnetic resonance spectra recorded at low fields ($\leq 2.3T$) show an almost complete overlap of sorbitol buffer peaks (4.3-4.7 ppm) with the water peak (4.6 ppm). Any light-induced changes associated with oxygen evolution are expected to occur in the water peak, so the overlap makes it difficult to measure and interpret the changes. The difficulty is readily overcome by recording spectra at high magnetic fields (Figure 1a). The resolution observed at 360 MHz for these systems is considerably better than at 220 MHz.

However, in systems such as thylakoid vesicles and algae, which can be resuspended without 0.4M sorbitol, interference can be reduced by choosing an appropriate buffer such as 40 mM NaHCO$_3$/D$_2$O(pD 7.0). Examples are shown in Figures 1b and 1c. Some inhomogeneity broadening remains because of algae and chloroplasts in the suspensions. Nevertheless, the resolution obtainable with a single rf pulse for these systems (~2 Hz in a suspension of 600 µg chlorophyll/ml) is sufficient for the reproducible observation of flash-induced changes in the spectra. Further line narrowing can be readily achieved with the well-known Carr-Purcell-Meiboom-Gill, or the Ostroff-Waugh pulse sequences. We have used the latter to observe $T_2^*$ of the non-exchangeable protons in thylakoid membranes.

In the second line of approach to photosynthetic systems by high-field NMR, we observed at 24.5 MHz the $^{35}$Cl spectra of chloroplast pellets in buffered NaCl solutions on a home-built high-resolution instrument. Isolated chloroplast thylakoids from certain salt-tolerant plant species require high chloride concentrations for $O_2$ evolution activity in vitro. Typical $^{35}$Cl lineshapes for these (halophyte) thylakoids in the presence of 1 M NaCl are given in Figure 2. The pH dependence of $1/T_{2}^*$ was found to be related with that of $O_2$ evolution.
in the pH range of 6.2 to 8.5 (Figure 3). Broadening of the $^{35}$Cl line is indicative of Cl$^-$ binding and this is observed in the pH range where maximal O$_2$ evolution occurs. These results suggest that in chloroplasts which require a high concentration of Cl$^-$ for O$_2$ evolution, reversible pH dependent binding of the Cl$^-$ is necessary to activate the O$_2$ evolving complex.

Please credit our contribution to the account of Professor H. S. Gutowsky. This work was carried out in collaboration with Professor Govindjee of the Departments of Botany and Physiology and Biophysics of the University of Illinois, and is supported by NSF grant PCM 79-11148 to HSG.

The use of a High-Q $^{35}$Cl NMR probe built by David Wright in the School's NMR lab is gratefully acknowledged.

Sincerely yours,

Ion C. Baianu
Christa Critchley
William Coleman

Departments of Botany and Physiology and Biophysics

cc: Prof. H. S. Gutowsky
    Prof. Govindjee
High-Field Proton Magnetic Resonance Spectra of Photosynthetic Systems

a. Suspensions of intact spinach chloroplasts in 400 mM sorbitol/20mM HEPES buffer at pH 6.8 (-95% D2O)

b. Suspensions of spinach thylakoid vesicles in 40 mM NaHCO3/D2O (pH 7.0, thylakoid membranes contained ~4Mn per PSII trap)

c. Suspensions of Chlamydomonas algae in D2O (pH 7.0)

Chemical shift/ppm from Me4Si

FIGURE 1.
$^{35}$Cl NMR of Mangrove Chloroplast Pellets: pH Dependence

**Figure 2.**

- Pellet, pH 8.0
- Pellet, pH 7.0
- Pellet, pH 6.25
- Supernatant, pH 8.0

**Figure 2.**
PH-DEPENDENCE OF CHLORIDE EFFECT (1M NaCl) IN CHLOROPLAST PELLETS

$T_2$-RELAXATION ○ (HIGH-FIELD $^{35}$Cl NMR)

ELECTRON TRANSPORT □, △, ○ ($H_2O \rightarrow FeCN$)

$1/T_2$ (sec$^{-1}$)

PHOLES $O_2$-mg$^{-1}$ CHL$^{-1}$-h$^{-1}$

1M NaCl-Hepes buffer

FIGURE 3.
We produced these spectra—

**13C-Satellite Excitation Using "INADEQUATE"**

Expansion of the partial INADEQUATE spectrum of 5α-androstane, showing overlapping 13C satellites of carbon 8 and 10. Note the efficiency of center-band cancellation resulting from the hardware stability and the software flexibility of the XL-200 pulse programmer. Assignments shown are the result of the "COSMIC" automatic analysis program on the XL-200.

*A. Bax, R. Freeman and S. Kempe, JACS, 102, 4849 (1980).*

**Heteronuclear Correlated 2-D Coumarin**

Heteronuclear Correlated 3-D NMR on coumarin. Presence of a resonance indicates presence of a C-H bond. The sub-splittings along the proton direction are the homonuclear 1H-1H splittings, even though the experiment is 13C observed. The phase cycling employed in the pulse sequence allows quadrature operation in both frequency domains.

... on this Instrument— with existing software and accessories.*

Varian XL-200 Superconducting FT NMR Spectrometer.

We guarantee that you can do the same. See the reverse side of this page for more XL-200 information.

*The same hardware and software shipped to Varian owners throughout the world.*
Immediate delivery on pulse programmer capabilities!

If you're still waiting for a hard-wired pulse programming device to perform the NMR experiments you want, you just don't have an XL-200 Superconducting FT NMR Spectrometer.

If you do have an XL-200, you know that when we promised you pulse programming capabilities, you got them on delivery of your XL System. Because pulse programming, even of the most sophisticated sequences, is one of several operations you can perform using the standard software you receive with every Varian XL-200 purchase.

As an XL-200 owner, you can take advantage of such new sequences as INEPT and INADEQUATE (13C satellite excitation via double quantum coherence). Our ongoing series of software programs, known as the Pulse Sequence Library, also alerts you to the latest experiments as they are published.

Remember this: If you already own an XL-200 NMR Spectrometer, you have a "Pulse Programmer: It's the Acquisition Processor, which we've been shipping on the XL-200 orders since 1978.

The XL-200's Acquisition Processor has a direct disk interface, its own CPU, and memory for both program and data. These additional components free the main CPU for other tasks.

This means you can run new experiments, essentially, right after you read the original research, or after receiving a copy of the PASCAL code in either a Varian software update or in a new issue of the Pulse Sequence Library.

Send today for new instrument brochure and applications literature!

Act now to receive your copy of the new brochure on the XL-200 Superconducting FT NMR Spectrometer. This publication includes information concerning 2-D NMR, pulse sequence generation, dot matrix displays, new software capabilities, user-programming, and other valuable input for NMR spectroscopists.

A new Varian Applications Report, titled "Two-Dimensional NMR on the XL-200" is also available. So write or call now for your copies of this literature.

If you would like a Varian Sales Representative to visit, please contact the Varian Sales Office nearest you. A list of offices appears below.

Varian U.S. Sales Offices

CALIFORNIA ILLINOIS
9001 Raymont Blvd. 205 W. Touhy Ave.
Danvers, CA 90240 Park Ridge, IL 60068
(213) 925-3415 (312) 825-7772
375 Dixtal Circle (301) 772-3683
Los Alito, CA 90402
(415) 968-8141 MARYLAND
COLORADO
4165 Kipling, Suite 1W้นWhatridge, CO 80033
(303) 425-0413 MASSACHUSETTS
GEORGIA
6650 Powers Ferry Rd.
Suite 100 Los Altos, CA 94022
(404) 955-1332
Suite 300
Atlanta, GA 30339
(404) 955-1332 ILLINOIS
NEW JERSEY
205 W. Touhy Ave.
25 Hanover Hts.
Park Ridge, IL 60068 Pompton Park, NJ 07932
(312) 825-7772 (201) 822-3700
MARYLAND
TEXAS
4701 Lydall Drive
6499 Riddings Rd.
Cheverly, MD 20781
SYRACUSE, NY 13206
(301) 772-3683 (315) 437-6494
MICHIGAN
NEW YORK
3721 W. Michigan
5750 Brentwood Dr., Suite 202
Suite 100
Lansing, MI 48917
Atlanta, GA 30339
(517) 327-5000 (713) 783-1800
GEORGIA
NEW YORK
6650 Powers Ferry Rd.
Suite 100
Los Altos, CA 94022
(404) 955-1332
6499 Riddings Rd.
(415) 968-8141
(315) 437-6494
4701 Lydall Drive
6499 Riddings Rd.
(301) 772-3683
(315) 437-6494
Cheverly, MD 20781
SYRACUSE, NY 13206
(301) 772-3683 (315) 437-6494
MICHIGAN
NEW YORK
3721 W. Michigan
5750 Brentwood Dr., Suite 202
Suite 300
Lansing, MI 48917
Atlanta, GA 30339
(517) 327-5000 (713) 783-1800
GEORGIA
NEW YORK
6650 Powers Ferry Rd.
Suite 100
Los Altos, CA 94022
(404) 955-1332
6499 Riddings Rd.
(415) 968-8141
(315) 437-6494
4701 Lydall Drive
6499 Riddings Rd.
(301) 772-3683 (315) 437-6494
Cheverly, MD 20781
SYRACUSE, NY 13206
(301) 772-3683 (315) 437-6494
MICHIGAN
NEW YORK
3721 W. Michigan
5750 Brentwood Dr., Suite 202
Suite 300
Lansing, MI 48917
Atlanta, GA 30339
(517) 327-5000 (713) 783-1800
GEORGIA
NEW YORK
6650 Powers Ferry Rd.
Suite 100
Los Altos, CA 94022
(404) 955-1332
6499 Riddings Rd.
(415) 968-8141
(315) 437-6494
4701 Lydall Drive
6499 Riddings Rd.
(301) 772-3683 (315) 437-6494
Cheverly, MD 20781
SYRACUSE, NY 13206
(301) 772-3683 (315) 437-6494
MICHIGAN
NEW YORK
3721 W. Michigan
5750 Brentwood Dr., Suite 202
Suite 300
Lansing, MI 48917
Atlanta, GA 30339
(517) 327-5000 (713) 783-1800
GEORGIA
Dear Professor Shapiro,

The electric saturation of molecular alignment studied by NMR

Quadrupole line splittings in the $^2$H and $^{14}$N NMR spectra of neat nitrobenzene-d$_5$, induced by an external electric field (E), were studied up to very high field strengths ($E = 1.8 \times 10^7$ V m$^{-1}$). The spectra were recorded on a Bruker WH 180 WB NMR spectrometer operating at a $^{14}$N frequency of 13.01 MHz and a $^2$H frequency of 27.64 MHz. The line splittings were measured in an electric field cell [1] with an electrode distance of 3 mm for the $^{14}$N experiment and 2.5 mm for the $^2$H experiment.

The magnitude of the line splitting ($\Delta \nu$) for the para $^2$H and $^{14}$N nuclei in nitrobenzene-d$_5$ is

$$\Delta \nu = \frac{3}{2} \left( \frac{e^2 qQ}{h} \right) < \frac{3}{2} \cos^2 \theta - \frac{1}{2} > E$$

with $e^2 qQ/h$ the quadrupole coupling constant (q.c.c.) of the nucleus concerned (q.c.c. $^2$H = 190 kHz, q.c.c. $^{14}$N = 1.520 MHz), and $\theta$ the angle between the molecular dipole moment $\mu$ and the electric field $E$. The term $< \frac{3}{2} \cos^2 \theta - \frac{1}{2} >$ is the molecular alignment. From Boltzmann statistics it follows that the theoretical alignment depends only on even powers of $E$. 


In the figure experimental $^{14}\text{N}$ line splittings are given as a function of $E^2$. At moderate fields the line splittings are proportional to $E^2$. Line 1 is a linear fit, $\Delta v = \frac{3}{2}(\text{q.c.c.}) c_2 E^2$, to the data points, including the origin, up to $E = 6.3 \times 10^6 \text{ V m}^{-1}$ with $c_2 = (6.38 \pm 0.02) \times 10^{-18} \text{ V}^{-2}\text{ m}^{-2}$. The same fit to the experimental $^2\text{H}$ line splittings gives $c_2 = (6.16 \pm 0.02) \times 10^{-18} \text{ V}^{-2}\text{ m}^{-2}$. With increasing electric field, $E > 6.3 \times 10^6 \text{ V m}^{-1}$, the line splittings deviate more and more from the calculated line 1, due to higher order electric field effects. Line 2 in the figure is a polynomial fit, $\Delta v = \frac{3}{2}(\text{q.c.c.}) (c_2 E^2 + c_4 E^4)$, to all the $^{14}\text{N}$ data points with $c_2 = (6.40 \pm 0.02) \times 10^{-18} \text{ V}^{-2}\text{ m}^{-2}$ and $c_4 = (-1.32 \pm 0.08) \times 10^{-33} \text{ V}^{-4}\text{ m}^{-4}$. The same polynomial fit to all $^2\text{H}$ data points gives $c_2 = (6.25 \pm 0.01) \times 10^{-18} \text{ V}^{-2}\text{ m}^{-2}$ and $c_4 = (-1.43 \pm 0.05) \times 10^{-33} \text{ V}^{-4}\text{ m}^{-4}$.

It is clear that higher order electric field effects have to be invoked to explain our experimental results. The phenomenon can be related to the electric saturation: the change of the permittivity in a strong electric field. Nitrobenzene has been reported to exhibit an anomalous saturation effect of the permittivity [2], but the saturation of the molecular alignment appears to be normal.

References:

Yours sincerely,

C. MacLean
F.J.J. de Kanter
T.M. Plantenga
LABORATORY MANAGER - CHEMICAL INSTRUMENTATION

A growing instrumentation facility seeks responsible director for position involving departmental instrument operations, training and supervision of operators, maintenance direction, and collaboration with faculty for research development and submission of major instrumentation proposals.

Applicants should have graduate training and experience in High-field FT-NMR or mass spectroscopy. An advanced degree in Chemistry or Physics is preferred, but candidates with equivalent experience will be considered. Experience in electronic and mechanical trouble-shooting is very desirable. This is a permanent position with competitive salary and fringe benefits ($25,000-30,000).

Applicants should submit a resume and have three letters of reference sent to Dr. Richard Lintvedt, Department of Chemistry, Wayne State University, Detroit, MI 48202. (313) 577-2591. Equal Opportunity/Affirmative Action Employer.
Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas  77843

Use of Lanthanides to Distinguish Meso and Racemic Forms

Dear Barry:

It should come as no surprise to learn that most of us in the pharmaceutical industry have been involved in optical purity determinations using the chiral shift reagent technique. We recently were confronted with an unusual request of a reverse nature. We were asked if we could tell whether a synthetic preparation of dimethyl-a,a'-bisphthalimido sebacate was the meso or racemic form.

Although it seemed unlikely that lanthanide treatment would provide an answer to this question, the problem nevertheless provoked a discussion as to what we might expect to see assuming that the enantiomeric methoxyl signals could be resolved. Given the physical separation of the sites for complex formation, it was not clear whether the two forms would behave differently in the presence of the reagent. Curiosity got the better of us and the results illustrated in the accompanying figure indicated that the optically inactive species are indeed resolvable. Inset A represents the enantiomeric methoxyl signals in the presence of about one molar equivalent of Eu(hfbc)_3, which established that the sample is roughly a 4:1 mixture of the meso and racemic forms. As expected, only diastereomeric separation of the methoxyls was evident in Eu(FOD)_3-treated material (inset B). X-ray analysis on a fractionated specimen identified the major component as meso.

It is a point of interest that in the absence of lanthanide neither the proton (300 MHz) nor carbon-13 spectrum provided evidence for a diastereomeric mixture.

Sincerely yours,

/\ah

Byron H. Arison
Figure: 300 MHz Spectrum of Dimethyl-α,α'-bishthalimido Sebacate
Dear Barry,

INDUSTRIAL NMR USERS' MEETING

A meeting was held at the Shell Research Laboratories in Amsterdam on December 10th 1980 to discuss the current interests and future needs in NMR in the industrial environment. Almost thirty spectroscopists from industrial laboratories in Europe, and representatives from the major NMR instrument manufacturers were present. The meeting had been convened because of a general feeling that manufacturers have so far received more feedback from universities than from industry and have therefore tended to cater more for the academic requirements, despite the fact that at least half the NMR instrumentation (in Europe) is present in industrial laboratories. One clear conclusion from the meeting, for example, was that the industrial user would much prefer a higher reliability of his spectrometer to still higher magnetic fields.

The main conclusions of the meeting were that there are a number of areas of urgency where manufacturers could provide immediate assistance and other areas where there was considerable interest and potential on a longer term basis. Of the urgent items, the need to improve the quantitative performance of NMR was stressed by almost all the participants. The comparison between the relatively inefficient NMR software and plotting routines and the more sophisticated infrared and mass spectrometry systems was also made by a number of people. On the subject of hardware it was clear that industrial NMR has a need for automatic sample changing and automatic shimming. The coupling of separatory technique (LC, GLC) to NMR is already applied but commercial equipment is still lacking and very desirable.

As to the longer term items there was more scope for the imagination and topics such as correlation 2-D NMR spectroscopy, spin imaging, routine NMR of solids and low cost FT NMR with permanent magnets were some of the interesting points raised.
All the participants received a report of the meeting, a summary of which was published in "European Spectroscopy News" 35 (1981) p. 53. This article has stimulated a good deal of interest from non-participants who are either new in the field of NMR, intending buying new equipment, anxious to find new applications or simply keen to maintain an awareness of the dramatic growth in industrial applications of NMR.

A follow-up meeting is planned for early 1982. Any TAMU NMR readers who might be interested in attending or wishing to receive a copy of the full report should feel free to write to me.

Whether or not this letter constitutes an official TAMU NMR contribution will become clear, I suppose, when we receive our next blue reminder!

Yours sincerely,

KONINKLIJKE/ SHELL-LABORATORIUM, AMSTERDAM

(A.D.H. Clague)

Re: Postdoctoral Position

Dear Barry:

There is a postdoctoral position in my group in the general area of NMR line-shape analysis and organometallic chemistry. The work involves a combination of synthesis of organolithium compounds and the study of their dynamic behavior using $^6$Li and $^{13}$C NMR line-shape analysis.

The person who accepts this position will also help maintain our home-built "Brukarian" multi-nuclear NMR spectrometer. We also have access to departmental instruments- Bruker WH-300, WH-80 and HX-90.

Interested persons should arrange to have three letters of recommendation sent to me on their behalf.

Sincerely yours,

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

Re: Cd NMR of Supercooled Solutions  

Dear Barry:  

After receiving your "Golden Letter" I felt I should pay the "price" of my subscription by describing some nice work that Professor Hans Jakobsen (of Aarhus, Denmark) and I have recently completed concerning the assignment of the Cd nmr spectrum of a supercooled solution of cadmium-glycine complexes recently reported by the Ackerman’s [M.J.B. Ackerman and J.J.H. Ackerman, J. Phys. Chem. 84, 3151(1980)]. The accompanying figure depicts the natural abundance Cd nmr spectra of -40°C supercooled aqueous (D$_2$O/H$_2$O, 1:1) solutions of 0.1M Cd(ClO$_4$)$_2$ and 0.25 glycine in SM NaNO$_3$ at pH 7.0. The spectrum in (a) was obtained using 95% N-enriched glycine and 2300 accumulations; expansions of the doublet and triplet for the resonances C and D are inserted. Spectrum (b) was obtained using isotopically normal glycine and 1000 transients. Gated $^1$H decoupling and a linebroadening of 20 Hz has been applied to both spectra. The spectra were obtained on the WH-400 via the South Carolina Magnetic Resonance Facility sponsored by the NSF.  

From the multiplicity of the Cd–N couplings in the figures one can deduce the assignments of the resonances. They are: Cd(II) “free”, Cd(II)Gly$^+$, Cd(II)Gly$_2^-$, and Cd(II)Gly$_3^-$ at -35.9, 53.6, 153.9, and 262.8, respectively. A brief report describing these experiments has been accepted for publication in the J. Phys. Chem. A limited number of preprints are available.

Warmest Regards,

Facility Director

Paul D. Ellis

The University of South Carolina: USC Aiken; USC Salkehatchie; Allendale; USC Beaufort; USC Columbia; Coastal Carolina College, Conway; USC Lancaster; USC Spartanburg; USC Sumter; USC Union; and the Military Campus.
School of Medicine G3
DEPARTMENT OF
BIOCHEMISTRY AND BIOPHYSICS

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

September 18, 1981

SQUARE TO SINEWAVE CONVERTER

Dear Barry:

In the design of a multi-frequency lock system for our simple NMR machine one electronic problem (among others) reared it ugly head: Our Syntest Frequency Synthesizer puts out a squarewave but we need a sinewave at any chosen frequency, as required by the system’s RF phase shifter. The solution to the problem may be of general interest.

An RC filter with fixed values of Rand C would work, except that the output amplitude would depend on frequency. In this circuit however C is a varactor whose value is automatically controlled by a feedback voltage derived from the output amplitude. Two stages of RC filtering and therefore two varactors are needed to get a good sinewave.

In somewhat more detail (see figure): The first Rand C are the 2.7K ohm resistor and the first varactor. Their output is a sawtooth of smaller amplitude than the input squarewave. After the second varactor the signal has become a good sinewave. Q2 and Q3 amplify this signal for the output. At an output voltage threshold of 0.6 Vpp the 1N914 and Q4 and their circuitry produce an AGC voltage which stabilizes the output level. The varactor impedances are made to be about 500 ohms at any frequency. The circuit as shown works at least from 3 to 25 MHz. Smaller varactor capacitances and/or smaller R’s would be required for higher frequencies.

Please credit this to Dr. M. Cohn’s subscription.

Sincerely,

James L. Engle

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

Dear Dr. Shapiro,

Enclosed is the schematic diagram for a simple pulse field gradient circuit. The circuit works extremely well for moderate gradient currents. The circuit is also inexpensive and easy to construct.

The most important elements in the circuit are the P-N-P Darlington-connected silicon power transistors\(^1\). These transistors allow switching of continuous currents to 5A and peak currents of 8A. The Darlington pairs are switched via the 74LS05 open collector inverters. The current through the gradient coil is determined by the combined resistances of the current limiting resistor and the gradient coil. A rotary switch and several different limiting resistors may be used to obtain switch selectable gradient strengths.

The rest of the circuit consists of logic gates to allow switching between two different gradient coils. A truth table describing the output of the circuit as a function of the input levels is shown with the schematic.

We have used this circuit in a new experiment for measuring diffusion constants. In this experiment the standard pulse field gradient technique is extended to multiple quantum NMR. An effective gradient strength twice as large as the actual physical gradient is obtained by working in the double quantum manifold. Complete results will be published in the near future.

Please credit this contribution to the subscription of Dr s.R.L. and R.R. Vold.

Sincerely,

Joel and Lyndsie

Joel F. Martin and Lyndsie S. Selwyn
Pulse Field Gradient Circuit

Inputs

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>L</td>
<td>Off</td>
<td>Off</td>
</tr>
<tr>
<td>L</td>
<td>H</td>
<td>Off</td>
<td>On</td>
</tr>
<tr>
<td>H</td>
<td>L</td>
<td>Off</td>
<td>Off</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>On</td>
<td>Off</td>
</tr>
</tbody>
</table>

\[ H = +5V \quad L = 0V \]

1. The Power Semiconductor Data Book, for Design Engineers, Texas Instruments Inc.
September 22, 1981

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

Two-D NMR of Solid Polymers

Dear Barry:

Because motions in solid polymers are complex, one needs a maximum of experimental data in order to study them. We have been interested in the analysis of $^{13}$C powder patterns, taken without magic-angle spinning, as one approach to getting as much information as possible. The fact that the samples are not spun has the additional advantage that variable-temperature studies are much simpler. A disadvantage is that one must generally use labelled materials in order to isolate the spectrum of a single carbon.

The upper spectrum in the figure shows the chemical-shift powder pattern for low-molecular-weight (~4000) bisphenol-A polycarbonate enriched at the carbonyl carbon. The spectrum is typical for a nonaxially symmetric carbon. Large distortions from motional effects are not obvious. Furthermore, very similar spectra are observed for samples containing various types of diluents. Thus, for this material, the powder pattern approach does not appear promising at first glance.

We are finding, however, that two-dimensional nmr techniques can help in the extraction of information. One of the simplest such experiments involves a two-D transformation of data from a simple Hahn spin-echo sequence. The bottom figure shows the contour plot of the resulting spectrum for the polycarbonate.

The linewidths in the vertical dimension may be considered to be the composite linewidths for all orientations leading to each of the chemical shifts indicated by the horizontal axis. The linewidths can be measured accurately from phased slices of the two-D spectrum.

Diluents added to the polymer change the observed linewidths and, in some cases, lead to spectra with varying linewidths across the chemical shift pattern. The overall results appear to contain information not only about dynamic rates but geometries of the motions.

We are also experimenting with various other two-D experiments for studying polymer motion, including some which are suitable for the study of $^{13}$C-$^{13}$C dipolar coupling powder patterns.
Professor Bernard L. Shapiro  
Texas A and M University  
September 22, 1981

Sincerely yours,

Mark Henrichs
Title: What one cannot do, two can do!

Dear Professor Shapiro,

We have studied NMR spectra of acetonitrile in a mixture of two thermotropic liquid crystals (of opposite diamagnetic anisotropies) namely, N-(p-ethoxybenzylidene)-p-n-butyraniline (EBBA) and Merck Phase ZLI-1167. At a particular concentration, the proton NMR spectra at 20°C, 21°C and 22°C are shown in the enclosed figure.

It is seen that the spectra at 20°C and 22°C show triplets due to dipolar interactions within the methyl protons of acetonitrile and the triplet spacings are in the ratio of nearly 1:2. At 21°C, however, two triplets are observed with splittings in the exact ratio of 1:2; the signs of the dipolar couplings are opposite. This is because at 22°C, the molecules orient like in EBBA whereas at 20°C, the orienting influence of ZLI-1167 dominates. At 21°C, both types of orientations are observed.

These experiments have been used to determine the proton chemical shift anisotropy without referring to a standard or without changing experimental conditions. The value for acetonitrile is found as -2.01 ± 0.01 ppm. The experiments have also been used to determine the indirect and the direct spin-spin couplings between heteronuclei separately. It may be emphasized that such an application has so far not been reported in the spectra of oriented molecules.

The details have been submitted for publication in the Chemical Physics Letters.

Yours sincerely,

C. L. Khetrapal  A. C. Kunwar

277-55
BANGALORE NMR FACILITY

Participating Institutions
Indian Institute of Science
Bangalore-560012
National Aeronautical Laboratory
Bangalore-560017
Raman Research Institute
Bangalore-560006
Tata Institute of Fundamental Research
Bombay-400085

Raman Research Institute
BANGALORE 560 080

Professor C.L.Khetrapal
Dr. A.C.Kunwar

Date: September 22, 1981

Ref:

Title: What one cannot do, two can do!
Proton NMR spectra of acetonitrile in the nematic phase of EBBE and ZLI-1167 at 270 MHz. The lines marked (•) arise from traces of water present in the solution.
Prof. B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
U.S.A.

Restrictions in 2D NMR

September 22, 1981

Dear Barry,

There appears to be a great deal of interest in 2D NMR at present, however it is a technique which requires a lot of instrument time. In the following tables I will show the effect of recycle time and spin coupling-chemical shift ratios upon the results obtained for three different 2D sequences. These should help to minimize experiment time and allow the spectroscopist to reject unsuitable spin systems.

Table 1. Pulse Sequence 90°-t₁-180°FID

<table>
<thead>
<tr>
<th>J/δ Ratio</th>
<th>System</th>
<th>Distortion of Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.039</td>
<td>Ethyl Bromide</td>
<td>None</td>
</tr>
<tr>
<td>0.061</td>
<td>Propionic Acid</td>
<td>None</td>
</tr>
<tr>
<td>0.094</td>
<td>2-Iodobutane</td>
<td>None</td>
</tr>
<tr>
<td>0.207</td>
<td>Tetraethylsilane</td>
<td>Significant</td>
</tr>
</tbody>
</table>

Recycle Time

<table>
<thead>
<tr>
<th></th>
<th>Ethyl Bromide</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 sec.</td>
<td>None</td>
</tr>
<tr>
<td>2 sec.</td>
<td>None</td>
</tr>
<tr>
<td>1.5 sec.</td>
<td>None</td>
</tr>
<tr>
<td>1.0 sec.</td>
<td>Slight</td>
</tr>
<tr>
<td>0.75 sec.</td>
<td>Moderate</td>
</tr>
<tr>
<td>0.5 sec.</td>
<td>Severe</td>
</tr>
</tbody>
</table>

+ Cr (AcAc)₃
T₁ ≈ 0.75 sec. and 0.47 sec.
Table 2. Pulse Sequence 90°-t₁-90°-t₁-FID

<table>
<thead>
<tr>
<th>J/δ Ratio</th>
<th>System</th>
<th>Distortion of Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Any</td>
<td>Any</td>
<td>None</td>
</tr>
</tbody>
</table>

Recycle Time

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3T₁</td>
<td>3-Bromo-4,5-</td>
<td>None</td>
</tr>
<tr>
<td>2T₁</td>
<td>dimethoxybenzoic Acid</td>
<td>Severe</td>
</tr>
</tbody>
</table>

Table 3. Pulse Sequence 90°-τ-90°-t₁-90°-FID

<table>
<thead>
<tr>
<th>J/δ Ratio</th>
<th>System</th>
<th>Distortion of Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Any</td>
<td>Any</td>
<td>Choose appropriate τ</td>
</tr>
</tbody>
</table>

Recycle Time

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3T₁</td>
<td>3-Bromo-4,5-</td>
<td>None</td>
</tr>
<tr>
<td>2T₁</td>
<td>dimethoxybenzoic Acid</td>
<td>Slight</td>
</tr>
</tbody>
</table>

Best wishes,

S. Brownstein

SB/dh
Dear Barry,

Tacticity of Poly(Vinyl Alcohol) from 100 MHz Carbon-13 NMR Spectra

A Bruker WM-400 high resolution nmr spectrometer with its superior resolution and sensitivity, compared with our lower field instruments is being used here in solving a variety of problems.

It had been found in earlier work that, in the 22.63 MHz nmr spectra of poly(vinyl alcohol) in solution, in D$_6$ dimethyl sulfoxide or in D$_2$O, the methine carbon atom resonance appeared as three peaks, showing sensitivity to triad tactic placements. The methylene carbon atom resonance appeared as four distinct peaks showing partial resolution into tetradts (1). More careful work at 22.63 MHz and spectra taken at 67.9 MHz showed further partial splitting of the methine carbon atom resonances into pentads (2).

This polymer has been re-examined using the WM-400 for $^{13}$C nmr at 100.62 MHz. As it was hoped, the greater chemical shift resolution leads to additional tactic sequencing information. The much higher sensitivity of the WM-400 allows extremely high signal-to-noise ratios to be obtained in overnight runs. This permits the use of resolution enhancement (Lorentzian to Gaussian conversion) while retaining good signal-to-noise ratios. The figure shows the methine carbon atom section of the 100.62 MHz $^{13}$C nmr spectrum of a D$_6$DMSO solution of poly(vinyl alcohol) obtained from an overnight run using resolution enhancement. All of the ten possible mm heptads are distinguishable in the 68 ppm region.

Yours sincerely,

Derick W. Ovenall

Please credit this contribution to the account of Dr. D. D. Bly.
100.62 MHz $^{13}$C NMR SPECTRUM OF POLYVINYL ALCOHOL
METHINE CARBON RESONANCES SHOW PARTIAL HEPTAD RESOLUTION
24.9.81

Professor B L Shapiro
Department of Chemistry
Texas A&M University
COLLEGE STATION
Texas 77843
USA

Dear Professor Shapiro

Helium Level Meter Modification

Apologies for the long silence from Edinburgh. This was due to the arrival of our new WM 300 WB for biological studies, and the need to get it going properly. I have now moved upstairs to look after it for Professor A I Scott and no longer have any connection with any other firm of NMR spectroscopists trading from the same address.

Other Bruker users will be interested in a potentially magnet preserving modification which Ian Francis, of Bruker Coventry, and I made to the helium level meter. This reconnects the 'low helium level' alarm siren to operate instead as a 'helium meter sampling' siren. In addition, the slow sampling position becomes infinitely slow, i.e., not at all. What happens now is that when the meter samples the siren sounds throughout the sampling period, thus making it most unlikely that the meter will be left on for longer than is necessary to take a reading of the level.

This modification was done after I inadvertently left the level meter on fast sampling over one weekend. Fortunately the magnet was almost full on the Friday, since by Monday the level was down to 11%.

The changes are very simple and all done on the helium meter p.c.b. I enclose the modified circuit diagram and some notes.

Yours sincerely

A S F Boyd

I Francis
Bruker Spectrospin
a) To prevent 'slow' sampling: disconnect 18 MΩ resistor from +15v supply and reconnect to earth on adjacent print area

b) To reconnect siren: remove +15v supply from pin 27 by cutting print track. Reconnect pin 27 to pin 16. Disconnect the 120Ω resistor from the op-amp LM 306 output and reconnect to earth on adjacent print area. The alarm on-off switch on the BCN 60 front panel should be left on
We recently installed two NTC-200 superconducting spectrometers. One of our applications of these systems has been the study of chain branching in polyethylene and ethylene-\(\alpha\)-olefin copolymers. We are especially interested in the accuracy and precision of the measurement of branches at levels of 1 to 2 branches/1000 C's in high density polymers (densities >0.95). To determine the precision of the analysis, two samples were run repetitively over several weeks. One sample had only ethyl branches and the other had only butyl branches. The samples were run as approximately 40% (w/v) solutions in dideuterotetrachloroethane. A typical spectrum is shown in Figure 1. The data was collected using 90° pulses and two sets of pulse delays -- 2.5s and 30s. The samples were not spun and 1000 transients were collected for each measurement.

The data are summarized in Table I where the average intensity (Int) of each peak, measured using peak heights, is given. These values are normalized to a total spectral intensity of 1000. The \(\sigma\) values give the standard deviation of these intensities for each peak for from 5 to 10 repeat runs. Ethyl branches were calculated using the average value of all peaks except that the Et-1 peak was ignored due to its long \(T_1\) when using the 2.5s delay data. Butyl branches were calculated using the average of all but the Bu-1 and Bu-2 peaks. The Bu-1 peak has contributions due to chain terminating methyls (note Int value at 30s delay) and Bu-2 has a long \(T_1\). The backbone carbon \(T_1\)'s were found to be 2.1 and 1.7s for samples A and B respectively. There is excellent agreement between the short and long delay branching data which indicates that by using selected resonances one can calculate branches/1000 C's in polyethylene without waiting 5 times the longest \(T_1\). This is due to the fact that most of the carbons near the branch have \(T_1\)'s similar to that of the backbone carbons.
### SAMPLE A (Et Branches)

<table>
<thead>
<tr>
<th>Peak T,</th>
<th>2.5s delay</th>
<th>30s delay</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Int</td>
<td>α</td>
</tr>
<tr>
<td>2.5s delay</td>
<td>30s delay</td>
<td>2.5s delay</td>
</tr>
<tr>
<td>α-Et/2</td>
<td>1.6</td>
<td>1.84</td>
</tr>
<tr>
<td>β-Et/2</td>
<td>1.7</td>
<td>1.88</td>
</tr>
<tr>
<td>C-Et</td>
<td>2.2</td>
<td>1.70</td>
</tr>
<tr>
<td>Et-2</td>
<td>1.7</td>
<td>1.92</td>
</tr>
<tr>
<td>Et-1</td>
<td>6.6</td>
<td>1.04</td>
</tr>
<tr>
<td>Branches/1000 C's</td>
<td>1.84</td>
<td>0.10</td>
</tr>
</tbody>
</table>

### SAMPLE B (Bu Branches)

<table>
<thead>
<tr>
<th>Peak T,</th>
<th>2.5s delay</th>
<th>30s delay</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Int</td>
<td>α</td>
</tr>
<tr>
<td>2.5s delay</td>
<td>30s delay</td>
<td>2.5s delay</td>
</tr>
<tr>
<td>α-Bu/2</td>
<td>0.8</td>
<td>1.97</td>
</tr>
<tr>
<td>β-Bu/2</td>
<td>0.9</td>
<td>1.76</td>
</tr>
<tr>
<td>C-Bu</td>
<td>1.3</td>
<td>1.81</td>
</tr>
<tr>
<td>Bu-4</td>
<td>0.8</td>
<td>1.89</td>
</tr>
<tr>
<td>Bu-2</td>
<td>3.1</td>
<td>1.16</td>
</tr>
<tr>
<td>Bu-1</td>
<td>6.5</td>
<td>1.00</td>
</tr>
<tr>
<td>Branches/1000 C's</td>
<td>1.86</td>
<td>0.10</td>
</tr>
</tbody>
</table>

---

**Figure 1.** $^{13}$C NMR Spectrum of a Polyethylene Sample Containing Ethyl Branches
September 21, 1981

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

TITLE: Position Available

Dear Barry:

We have a position available for an NMR Spectroscopist in the Analytical Research Section at the Eastern Research Center.

The successful candidate will be responsible for the overall operation of NMR laboratory at the research center with activities in many areas of organic and inorganic chemistry. Duties will include:

- Operation and maintenance of instruments (Presently a multinuclear Bruker HFX-90 and a PE 600)
- Providing structural information to support ongoing programs
- Advising researchers on applications of NMR and related techniques
- Developing new approaches of NMR and related techniques
- Advising the Center on future needs for capabilities including justifying acquisitions, selecting and acquiring new equipment

The requirements for the position include a Ph.D. or equivalent with a strong background and interest in NMR. Excellent communication skills and the ability to work closely with many different individuals are needed. We are an equal opportunity employer.

For further information, please contact the undersigned.

Sincerely yours,

D. H. Marr, Manager  
Analytical Research

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

Dear Barry:

This letter is written to enlist your aid in finding suitable candidates for a faculty appointment in nuclear magnetic resonance in our Department.

Our preference is for an appointment at the associate or full professor level, hence we seek names of individuals who have already demonstrated their capacity for organizing a vigorous research program and have given evidence of distinguish in scholarship and teaching. However, strong consideration will also be given to candidates at the threshold of their career who show exceptional promise. The exact area of their research is of secondary importance but we expect the person we add to interact strongly with the rest of the Department in continuing to build up our NMR facility.

At the moment our instrumentation consists of a 270 MHz wide bore Bruker spectrometer \((^1H, ^13C, ^15N)\) coupled with a Nicolet 1089 computer, a 150 MHz wide bore broad band spectrometer coupled to a Nicolet 1083 computer, a 90 MHz Bruker spectrometer \((^1H, ^13C, ^15C, ^17O, ^19F, ^31P\) with D2 lock option) currently being converted to operation in the FT mode with quadrature detection and two 60 MHz self-service instruments. Special features include side spinning probes and a CP-MAS solid capability under construction for the 150 MHz spectrometer; a data acquisition and processing network linking these and other spectrometers to be acquired eventually has been developed and is in the final stages of construction. Support personnel experienced in the design and construction of apparatus needed for the facility are on hand and we expect that funds will become available to develop these facilities further.

I hope that you have candidates to suggest for the position we seek to fill. If so, please write me or call me at (904)-644-2774. We appreciate your help.

Sincerely yours,

Werner Herz
Professor of Chemistry
Chairman, Search Committee
October 1, 1981

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

RE: Research Associate Position Available at
The South Carolina NMR Facility.

Dear Barry:

Just a short note to inform your readers of the immediate availability of a Research Associate Position in the NMR Facility. The salary for the position is $18,000 per year. It is expected that 50% of the individual's time would be spent with responsibilities associated with the facility (scheduling, working with outside users, developing special techniques within the facility, etc.) and the remaining time devoted to on-going research projects in my group.

Interested applicants should send a resume and two letters of reference to me, immediately.

We are currently finishing our initial experiments on $^{113}$Cd single crystals. When the results are in a more concise form, I will summarize them in another contribution.

Warmest Regards,

Paul D. Ellis
Professor of Chemistry and
Facility Director

PDE:tb
Nicolet Supercon FT-NMR Spectrometers
Uncompromising performance, limitless adaptability.

Our spectrometer systems have been conceived and designed to provide optimum performance while being fully adaptable to new techniques with minimal cost and difficulty. More than just a collection of instruments, they represent a completely modular approach to FT-NMR instrumentation that allows the user to expand his system as his research needs grow and to easily accommodate new experimental techniques as they develop.

Outstanding Nicolet features include these:
• A full range of superconducting magnets from 4.7T to 11.7T (200MHz to 500MHz proton frequency range), in both wide-bore and narrow-bore configurations.
• Multinuclear observation with a wide variety of fixed-tune and broadband probes.
• Simultaneous acquisition, processing, and plotting for greater sample throughput.
• Simplified control of spectrometer operations and parameters by using easy keyboard commands.

• Advanced Nicolet 1180E Data System with 128K/20-bit memory, 256-step pulse programmer, and the most comprehensive FT-NMR software package available.
• Extended dynamic range performance with 40-bit acquisition and floating-point processing.
• An expandable pulse-sequence library, including T1, T2, Redfield, INEPT, homo- and hetero-2D-FT, etc.
• Convenient computer control of field shimming, observe and decoupling frequencies, sample-temperature, and probe-tuning.

• Precise digital plotting with full annotation of spectral parameters and flexibility of hardcopy format.

The versatile Nicolet spectrometers provide the user with the ability to easily adapt to the newest techniques and experimental configurations. Some of these are:
• High resolution studies of solids with Waugh-Pines cross-polarization and magic-angle spinning.
• High sensitivity wide-bore 13C studies of high molecular weight polymers.
• Automated T1 and T2 measurements.
• Chemical dynamics studies.
• Temperature-programmed experiments.
• 31P experiments on living organs.
THE SOLID LEADER in NMR
With Multi-Nuclear/Multi-Field Solid State Probes

• High field solid sample probe for JEOL's 200 MHz SCM!
• Tunable heads — interchangeable plug-in matching units for observation of
  $^{13}$C (~50 MHz)
  $^{31}$P (~80 MHz)
  $^{29}$Si (~40 MHz)
  with one probe!
• Self starting rotor/stator design!
• High speed magic-angle sample spinning (>4.0 KHz)!
• "Magic lift probe" for quick sample change and probe insertion!
• All this, in addition to a full line of dual and broad-band high resolution liquid sample probes!

Low Cost/Low Field Solids Probe

Chemagnetics solids probe for JEOL's 60 MHz NMR.

• Solid sample probe for JEOL's 60 MHz CP/MAS FT-NMR.
• Best results for coal, shale oil & rigid polymers.
• Large sample size (~5cc).
• Probes available for observation of $^{13}$C, $^{31}$P and $^{29}$Si!

JEOL
235 Birchwood Ave., Cranford, N.J. 07016
201-222-8820