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

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FORTHCOMING NMR MEETINGS (Additional listings are solicited)
Second International Symposium on the Synthesis and Applications of Isotopically Labeled Compounds - September 3-6, 1985; Kansas City, Missouri; Dr. Donald Wilk, Symposium Coordinator, University of Missouri-Kansas City, School of Pharmacy, 5101 Rockhill Road, Kansas City, MO 64110-2499.

FACSS (Federation of Analytical Chemistry and Spectroscopy Societies) - September 29 - October 4, 1985; 12th Annual Meeting; Philadelphia, PA; Included are eight sessions on NMR. Contact A.H. Ullman, Procter & Gamble Co., 6250 Center Hill Rd., Cincinnati, OH 45242, 513-659-6445.

J.H. Goldstein Retirement Symposium - October 25, 1985; Emory University, Atlanta, Georgia; see page 23.


British Radiofrequency Spectroscopy Group Meeting - April 9-11, 1986; Oxford University, Oxford OX1 30G, England; see page 23.

C.S.R.-Brazil Symposium on Recent Developments in Organic and Bioorganic NMR - July 7-11, 1986; Campinas, Brazil; see page 59.

Suggestions for other types of articles, news items, etc., to appear in the Newsletter would be welcomed - please make your wishes known.

Advertisement

DEADLINE DATES
No. 325 (October) --- 27 September 1985
No. 326 (November) --- 25 October 1985

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.
Dear Professor Shapiro,

RADIATION DAMPING EFFECTS IN HIGH-FIELD NMR

Although the phenomenon of radiation damping has been known since the earliest days of NMR it can still cause the occasional surprise. Damping effects increase with the intensity of the signal involved and are therefore more prevalent with high-field spectrometers; they can also have different effects on the various components of a multi-line spectrum. A text-book example was observed at 500 MHz here when a 35 mol% ethanol/D$_2$O sample was prepared with the intention of testing some two-dimensional experiments. Instead of the expected well-resolved multiplets with binomial peak heights the spectrum shown in figure 1a was obtained. Clearly, the relative peak-heights within each multiplet and those between the two multiplets are far from binomial. A closer inspection shows that the line-shapes are also distorted with, for example, the outer lines of the triplet having a noticeably asymmetric shape and a somewhat smaller line-width than the central component. Radiation damping was conclusively identified as the culprit by the following observations:

(i) The carbon-13 satellite signals in the spectrum of figure 1a do have the anticipated binomial peak-heights and have lines which are narrower, more symmetric, and of nearly identical shape: one satellite is shown inset in figure 1.

(ii) If a spectrum is obtained with the probe grossly detuned the main ethanol signals also have narrow lines and the "correct" relative intensities, as shown in figure 1b.

![Figure 1a](image)

![Figure 1b](image)
Classically, for a single resonance radiation damping can be attributed to an oscillating magnetic field which tends to rotate the magnetization vector towards the equilibrium position. The source of this field is the circulating current induced in the probe's tuned circuit by the transverse component of the magnetization vector itself. De-tuning the probe reduces the magnitude of the current and so also reduces the damping (hand-in-hand with the signal-to-noise ratio): this is the traditional test for radiation damping. Even when the probe is properly tuned the carbon-13 satellite signals are not materially affected by radiation damping as these signals are too weak to operate significant reaction fields themselves and the fields due to the parent peaks, although much more intense, are off-resonance by an amount which is large relative to their magnitude.

The reduction in damping which is obtained by detuning the probe can be put to good use for shimming samples which have an intense solvent peak, a situation that arises whenever substances are to be studied in aqueous solution. Optimizing the field homogeneity by observing a free induction decay is easier and quicker than looking at a deuterium lock level but is only practicable if the observed decay is dominated by magnetic field inhomogeneity. For many samples which have a strong solvent resonance this can be ensured simply by detuning the probe to the point where radiation damping is insignificant. The solvent signal can then be used for shimming and once the required homogeneity has been obtained the probe can be returned for maximum sensitivity. An extreme but not uncommon example of the effects of probe-tuning on a 90% H2O signal is shown in figure 2: the FID shown is part a of the figure was obtained after shimming with the probe greatly detuned and corresponds to a line-width of 0.5Hz, whereas once the probe is returned the signal decays much faster (figure 2b) and the line-width increases to nearly 15Hz.

Regards,

T. Frenkiel
June 4, 1985

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

Dear Professor Shapiro:

COSYER

Occasionally, excessive $t_1$ noise, due for example to a solvent peak, obliterates the crosspeaks at $(\alpha_A, \alpha_B)$ in a pure phase 2D-COSY experiment. In this case better digital resolution is needed in $\alpha_1$ in order to measure coupling constants on resonance B accurately from the $(\alpha_B, \alpha_B)$ crosspeak. There is a simple way to do this without having to accumulate any more $t_1$ slices. It involves a modified COSY experiment, which we have dubbed COSYER (COSY with Expanded $\alpha_1$ scalar coupling Resolution). The pulse sequence is:

$$90^\circ - \left( \frac{\tau_1-180}{2} - \frac{\tau_1}{2} \right) 90^\circ - t$$

An additional period, $\frac{(\tau_1-180-\tau_1)}{2}$, is included which varies with $t_1$. This period refocuses the chemical shift but not the scalar coupling. Hence when processed, the experiment has an apparent doubling of all coupling constants in $\alpha_1$ without affecting the chemical shift dispersion. Systematic errors in coupling constant measurement in the $\alpha_1$ dimension are thus decreased by a factor of two.

In the Figure a normal COSY experiment (A) is compared to a COSYER experiment (B). Five hundred twelve $t_1$ values were accumulated. The final data matrix after processing was 1K by 1K. The doubling of the apparent scalar coupling constant in $\alpha_1$ is quite obvious in the COSYER spectra.

The major shortcoming of the experiment is a decrease in signal-to-noise due to the increased length of the modified $t_1$ period. This tends to negate any signal-to-noise improvement one might expect from reduced cancellation of antiphase components for crosspeaks with small coupling constants.
Sincerely yours,

Stephen Festik

R. Gampe

E. Olejniczak

E. Zuiderweg

SF/RG/EO/EZ:cd
Sensitivity of Two-Dimensional NMR as a Function of Field Strength

Dear Barry:

While working on a budget justification for a grant proposal, I decided to include a description of the sensitivity of two-dimensional NMR as a function of field strength. Since I did not remember ever seeing such a calculation, I decided doing it was easier than going to the library. If we consider the case of going from 200 to 400 MHz with a two-fold gain in intrinsic sensitivity (in a one-pulse experiment), then the total time for a 400 experiment will consist of one-fourth as many transients for each increment of $t_1$ but twice as many increments of $t_1$ for equal resolution. Thus, the sensitivity is given by:

$$\text{sensitivity} = \left(\frac{\text{ratio of intrinsic sensitivity}}{\text{ratio of B fields}}\right)^{1/2}$$

Since the intrinsic sensitivity is known to increase with the 3/2 power of the field, the theoretical limit for increase in sensitivity of two-dimensional NMR with field strength is merely linear. Since the increases in intrinsic sensitivity are never quite up to the theoretical limit, the actual gains in two-dimensional NMR sensitivity tend to be about $B^{3/2}$. Nevertheless, the dispersion of the two-dimensional data does go as $B^2$.

Sincerely,

Philip Bolton
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July 21, 1985

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

Dear Barry:

In response to your request I'm providing a summary of our recent results on measurement of pK's in THF using $^{13}$C nmr spectra from an FT-80. Though this may be considered a mundane application of nmr, I think the numbers obtained will be of interest to the organic chemists amongst us.

*What 'request', Bob?

Yours sincerely,

R.R. Fraser

RRF:cmg

Departement de chimie
Faculte des sciences et de genie
365 Nicholas
X1N 9B4

Department of Chemistry
Faculty of Science and Engineering
< 15.7°

\textsuperscript{\#} represents pH of rearranged isomer, o-cyanophenol
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In vivo $^{31}$P NMR study of dose dependent tumor response to X-irradiation.

Localised $^{31}$P NMR spectroscopy gives information about tissue metabolism and might therefore be used to study tumor response to therapy in animals and humans. In collaboration with the department of Radiotherapy, University Hospital Utrecht (Paul Sijens) we investigated this possibility by studying the response of subcutaneously implanted murine mammary carcinomas NU 82 to 10 and 20 Gy gamma radiation. 48 mice were studied during 2 days by in vivo $^{31}$P NMR at 7.7 T. Tumors with an average mass of 1.5 g in the flank of the animals were measured using solenoidal coils, in a way analogous to the one described by Evanscho e.a. Magn.Reson.Med.1, 508 (1984).

Results are shown in the figure. During the time of observation no change in intracellular pH (as derived from the chemical shift of the P peak) and tumor size was observed. Untreated tumors increased 30% in volume during that time.

As appears from the figure, treatment with a dose of 20 Gy induced metabolic changes to the murine tumor NU 82 which differed significantly from the 10 Gy dose treatment. Studies are now in progress to explain the observed spectral changes.

Dr. W.M.M.J. Bovee

Dr. P.Sijens

Please credit this contribution to professor J.Smidt.
Figure IA: In vivo $^{31}$P NMR spectra of tumors NU-82 of different size: each spectrum took 7 minutes. Peak assignment; 1: phosphomonoesters, 2: inorganic phosphate, 3: phosphodiesters, 4: phosphocreatine, 5: γ-ATP, 6: α-ATP, 7: diphosphodiesters, 8: β-ATP.

Figure IB: The ratio ATP/Pₐ after radiotherapy with a dose of 10 and 20 Gy as a percentage of the value before treatment, plotted versus time. Bars indicate the standard error of the mean.
The linear pentadecapeptide gramicidin A (GA) forms ion permeable channels in biological and artificial membranes. The problem of the channel conformation is dramatically complicated by diversity of energetically allowed conformations of GA. Although the dimeric nature of the GA channel is established, still numerous forms of both single- and double-stranded helices have to be considered.

We made use of 500 MHz 2D NMR (COSY, NOESY, RELSY, NOERELSY, 2QT) for conformational analysis of \([\text{Val}^1]\text{GA}\) and its metal complexes in different milieu. In dioxane solution GA forms four basic conformational species (1). The species 3 was isolated and demonstrated to be a left-handed antiparallel double helix \(\frac{\pi}{\pi} \text{LD}_{5.6}\) with 5.6 residues per turn (2). The species 4 was represented by synthetic analog des-3,4,5,6 [Val\(^1\)]GA, which forms a right-handed parallel double helix \(\frac{\pi}{\pi} \text{LD}_{5.6}\) in dioxane (3). The conformation of the caesium-GA complex 1:1 in mixed methanol–chloroform solvent is a right-handed antiparallel double helix \(\frac{\pi}{\pi} \text{LD}_{7.2}\) (4) which has proper luminal diameter (~0.4 nm) of the central axial cavity to incorporate Cs\(^+\) cations. Although these double helical structures of GA meet general requirements of the transmembrane channel, the direct NMR study of GA in detergent micelles demonstrates crucially different structure.

GA was incorporated into sodium dodecyl sulphate (SDS) micelles by dropwise addition of the 2,2,2-trifluoroethanol-D\(_3\) (TFA) solution of GA into SDS-D\(_{25}\) dispersion in H\(_2\)O or D\(_2\)O. The final condition (5 mM GA and 0.25 M SDS-D\(_{25}\) in 16:1 water/TFA, molar ratio) corresponds to incorporation of not more than two GA molecules into one micelle. CD spectrum of GA in SDS micelles is identical to those of GA in dipalmitoyl phosphatidylcholine liposomes and lyssolecithin micelles. The \(^1\)H-, \(^7\)Li-, \(^{13}\)C- and \(^{23}\)Na-NMR spectra prove that GA in SDS micelles interacts with alkali metal cations.
(Li⁺ or Na⁺). Results of the proton 2D NMR spectroscopy, model building and further refinements by means of conformational energy minimization demonstrate that the molecular structure of the Na⁺-GA complex in micelles is a head-to-head \( \overset{\frown}{6.3} \overset{\frown}{6.3} \) dimer (See Figure), formed by two right-handed single-stranded \( \overset{\frown}{6.3} \) helices with 6.3 residues per turn. The dimer of \( \sim 2.6 \) nm length has \( C_2 \) symmetry axis perpendicular to the channel axis. The conformation of GA transmembrane channel differs from the structure proposed by Urry et al. (5) in handedness of the helices.

With kind regards,

Sincerely yours,

Vladimir Bystrov and Alexander Arseniev


Na⁺-gramicidin A in SDS: \( \overset{\frown}{6.3} \overset{\frown}{6.3} \)
June 27, 1985

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

"Broadline NMR Probe Construction at IUPUI"

Dear Professor Shapiro:

We intend to enter the realms of broadline NMR at IUPUI. Although construction of a homebuilt broadline machine is underway, initially we shall attempt to use Durgu Rao's Nicolet NT-300 high resolution spectrometer.

The $^2$H NMR spectrum shown below represents the first test of a homebuilt probe. The probe is a horizontal mounted coil (9 turns 18 AWG wire, 1 cm length and diameter) with two Polyflon 0.8-10 pf variable capacitors for tuning and matching. The S/N is 10 for 32 scans on natural abundance $^2$H in water which, given the poor homogeneity of the spectrum, is not too bad. The $\pi/2$ pulse width of $\sim 9$ µs (200 w rf power) needs improving. Bigger (wider) and better things (spectra) will hopefully follow.

Yours sincerely,

Bruce D. Ray

Stephen R. Wassall

Please credit this contribution to
July 11, 1985

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

Dear Professor Shapiro:

Plotter Modification on the QE-300

We have finally caught up with our NMR backlog by turning all of our routine proton and carbon requests over to a GE QE-300 with an automated sample-changer. We have had some struggles getting the thing to go, but we are now fairly pleased with the results--one instrument has replaced three (1H on an automated T-60, 2H on a WM270, and 13C on an FT-80), and one person handles the samples which formerly took two persons plus a lot of overtime hours. The sample-changer will hold up to 99 samples, and we have run queues of 60 or more tubes on several occasions.

One problem that has occurred from time to time is that we arrive in the morning to discover that the queue has been completed, but unfortunately the paper on the plotter jumped off track during the run, leading to useless plots for all subsequent samples. The cause for this disaster seems to be that the paper is being pulled back and forth so rapidly that it sometimes flips off of the sprockets of the ZETA-8. We have been able to recall the stored FIDs and to spend the day retransforming and replotting, but I have finally cured the problem by the following modification (well, it hasn't happened again since I installed the adaptor on May 20, anyway).

The prototype device is made of cardboard, but we plan to cut a new one out of something prettier.

This device forces the Z-fold paper to stay down near the sprockets at all times, but it does not get in the way when several folds of paper are suddenly sent out the back by an RZ command, for example. We have never actually been present when the paper has gone off track, so we can't describe exactly how it happens. We have seen the results several times however, and this device seems to eliminate them effectively. If anybody else with a ZETA has the same problem, I recommend that you find a cardboard box and a sharp knife and go to work!
Back view of ZETA-8 with adaptor installed

Folded inside the ZETA, on top of the wire or spring paper guide

Taped to outside of ZETA-8

Sincerely,

LILLY RESEARCH LABORATORIES

Ann H. Hunt, Ph.D.
Research Scientist
Physical Chemistry Research
Now, with the new GN Series high resolution NMR spectrometers, GE brings you the greatest versatility in multinuclear liquids and solids research ... and backs it up with GE's unequalled quality, reliability, and continuous support.

GE is committed to providing you with the highest performing NMR systems today and in the future. With the GN Series, available at various field strengths and bore sizes, you can perform simple one-pulse analysis, or complex state of the art experiments like triple quantum correlation and various selective excitation experiments through the system's automated hardware features which include:

☐ A comprehensive observe and decoupling phase shifter for < 90° phase shifts.
☐ Complete computer gain control of lock observe and proton/x-nucleus decoupler channels.
☐ A new, super-sensitive deuterium lock.

The Spectrometer Control Processor is easily controlled by GEM, the latest generation of NMR software. GEM-users can direct the GN system to perform a complete series of predetermined experiments for total sample analysis — or take control of individual components and develop their own custom NMR analysis.

With a variety of accessories including array processor, x-nucleus decoupler, liquids probes and six different solids probes with unique capabilities, and a choice of data storage devices, your GN spectrometer can give you an ultimate advantage!

Step into the future with GE. We're ready to assist you with expanding support through our toll-free 800 customer service number. To receive a comprehensive new GN Series brochure or arrange for a demonstration, call (415) 490-8310, or write General Electric Company, NMR Instruments, 255 Fourier Ave., Fremont, CA 94539.
July 24, 1985

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

Dear Barry:

Postdoc Position; Ionic Strength Affects Cytochrome c Proton NMR Spectra

In the course of recent studies involving the molecular redox/docking complex between cytochrome c's and cytochrome c peroxidase we noticed that proton NMR spectra of cytochrome c exhibited a dependence upon the salt concentration of the protein solution. The accompanying spectra indicate that quite severe shifts are encountered, ranging up to 0.7 ppm for several hyperfine shifts. We have also observed significant linewidth variations in the hyperfine shifts as a result of different salt concentrations. I bring this to readers' attention for several reasons. Cytochrome c is, perhaps, the heme protein that has been most commonly studied, however cytochrome c peroxidase also exhibits this effect and it may be general. Studies that include pH dependence must be acknowledged to involve alteration in the ionic strength of the protein solution so that observed shifts may be due, in part, to changes in ion concentrations.

On a different topic, beginning September 1, 1985, I shall have a postdoctoral position available for one to five years. The person I am seeking should be capable of performing modern NMR experiments and will do work on NIH funded research involving small heme proteins. My lab currently consists of two graduate students working on the same project as this postdoc will, and a second postdoc working on an NSF supported project. Our lab is very well equipped for modern biochemistry and my group has access to a newly installed GE 360MHz spectrometer for 25 days per month, on the average. The spectrometer has a wide bore magnet, is completely broadband, has an X-nucleus decoupler, an array processor and a 96 Mbyte CMD disc drive. UNM is an equal opportunity, affirmative action employer and interested people should write to me or call me collect at (505-277-3621).

Sincerely,

James D. Satterlee

DEPARTMENT OF CHEMISTRY  TELEPHONE 505: 277-6655
361 MHz proton NMR spectrum of 2.5 mM cytochrome c (horse), pH=7.3. The full spectrum is of a solution in 0.300 M KNO₃. The inserts show the differences in selected regions between (A) 0.300 M KNO₃ and (B) 0.00 M KNO₃ solutions of this protein. In each case the temperature was 23°C.
PROFESSOR J. H. GOLDSTEIN'S RETIREMENT SYMPOSIUM

Prof. J. H. Goldstein is retiring at the end of 1985 after a long and distinguished NMR career at Emory University, Atlanta, GA. His former students are organising a one-day symposium to mark the occasion. It will be held in the Chemistry Building, Emory University, Atlanta, GA, on Friday, October 25, 1985. The program will include:

1. Roast and Boast Session
2. Several NMR presentations by his former students
3. After-dinner Symposium

All of Jake's colleagues, students and other NMR spectroscopists are invited to take part and make the event a memorable one. If anyone would like to make a presentation, scientific or otherwise, they are welcome to do so and they will be included in the final program.

Further information and details can be obtained by contacting:

Gade S. Reddy
CR&D - E328/129
Du Pont Experimental Station
Wilmington, DE 19898
Tel: (302) 772-3116 or 772-3738

British Radiofrequency Spectroscopy Group
Spring Meeting 1986
High Resolution NMR in Solids
Oxford, April 9-11, 1986

This meeting is designed to discuss recent developments in solid state NMR and to illustrate their applications in areas of research from biology and chemistry to materials science and technology.


For further details, please contact Dr. C.M. Dobson, Inorganic Chemistry Laboratory, South Parks Road, Oxford, U.K. OX1 3Q8, Tel. (0865) 53424.
June 19, 1985

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

Dear Professor Shapiro:

Re: Structure-Strength Relationships in PF Adhesives

The advent of color copying and the increasing use of pink papers to grab the reader's attention make me more exasperated—these materials are not recyclable and their use entails the waste of a valuable resource.

Dr. Robert H. Young and I have been pursuing PF resin cure chemistry in moderate detail since a CP/MAS study appeared last year (1). Bob's interest is dynamic mechanical analysis (DMA), which measures a strength modulus as a resin cures under carefully controlled conditions; my interest is in following cure structurally by CP/MAS NMR on our S-100; our mutual interest is whether the structure and strength measurements agree. The DMA modulus-time data resemble a titration curve, going from liquid resin (0% cure) up to a modulus plateau (100% cure). NMR samples can be taken at any DMA cure state; the integrated spectrum yields the amounts of strengthening structures (methylene bridges and dimethylene ether linkages), weakening structures (methyls, methylols and aldehydes) and total aromatic substitution. These also are convertible into % cure numbers, zero being the gelled liquid resin and 100 the terminal polymer.

Ideally, a plot of % cure (NMR) against % cure (DMA) will be linear. However (see figure), this occurs only at low curing temperatures; at higher temperatures, NMR cure leads, which confirms Bob's suspicion that the DMA modulus is partly canceled by thermal softening of the resin matrix, especially in the early stages, and that softening effects increase with temperature. Even though curing chemistry is going on, the DMA doesn't see it for awhile. Now we can calibrate the DMA (after we get some more data points in the figure) to compensate for softening effects in this resin system—others might need separate calibrations. We also will report later the reaction rates for formation of various linkages and groups.

Incidentally, I hear that Don Sawyer is joining up as Department Chairman; please relay my best regards.

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NEW ERA ENTERPRISES
P.O. BOX 425 • VINELAND, NJ 08360
PHONE: 609-794-2005
Dear Barry:

PHASE STRUCTURE DETERMINATIONS OF POLYETHYLENE USING $^2$H SPIN LATTICE RELAXATION STUDIES

As an initial contribution for my TAMU subscription, I thought that I would present some recent solid state $^2$H NMR spin lattice relaxation data. Polyethylenes are known from laser Raman work to exist in three distinct phases; crystalline (orthorhombic packing), interfacial (pseudohexagonal packaging) and amorphous (1). Since the chains in each phase experience different motions, the recovery of the $^2$H magnetization after saturation can be used to determine the phase structure of polyethylene.

A sample of linear, perdeuterated polyethylene was pressed as a thin film and then rapidly cooled. The sample magnetization was saturated with seven 90° pulses separated by 1 msec delays. After a variable delay, the spectrum was acquired with a solid echo, using 45° pulses, and phase cycling of the pulses.

Figure 1 shows the decay of the total magnetization with time as well as the mass fractions and $^2$H T1 values for each component. These values were extracted graphically and the solid line in Figure 1 is the calculated decay using these values.
FIGURE 1 - Decay of the $^2$H magnetization with time for a linear, perdeuterated polyethylene. The table contains the $T_1$ and mass fraction data. The insert is the fully relaxed spectrum.
The advantage of $^2$H NMR over $^1$H NMR, in studies of this type is twofold. First, spin diffusion is largely quenched in $^2$H NMR and second, $^2$H NMR gives well defined lineshapes (see insert to Figure 1). These lineshapes can give insight into the type and symmetry of the motions which are occurring in not only the amorphous and crystalline phases (2), but also the interfacial phase of polyethylene.

Yours truly,

DU PONT CANADA INC.

Eric Kelusky
Research Scientist


XL-200 Spectrometer for Sale

Dear Dr. Shapiro:

We are selling a Varian XL-200 which is in fine condition, which is equipped with a 5 mm proton probe, a 10 mm probe for $^{15}$N to $^{31}$P, a 16 mm probe for $^{15}$N to $^{31}$P, RS232 interface for digital plotters and high speed printers, a quarter wave preamplifier, about ten spare removable disks, and the user's programming materials. The spectrometer has been well maintained and is being sold to make room for a higher field spectrometer. I hope you will list this in your NMR newsletter.

Sincerely,

Albert J. Fry
Chairman and Professor
Department of Chemistry
How to improve magnetic field measurement and control

You can get a new standard of performance by upgrading your field regulation and measurement equipment. The superiority of advanced design field regulators and magnetometers from IBM Instruments can be seen clearly in the performance curves shown at the right. Regulator accuracy is 200mG from -50G to +23kG.

Microprocessors in each unit provide ease of operation and complete flexibility of application. Most units also can be programmed through RS 232 or IEEE 488 (IEC 625) interfaces. Other outstanding features include:

ER 031M Hall effect regulator—Low noise, 0.1mG rms in 1Hz bandwidth. Excellent long-term stability, 2 ppm/degree.


BH 15 Hall effect magnetometer-regulator—Combines features of ER 031M and ER 031Z plus sweep capability, digital and analog outputs and homogeneity plots (x-y) with resolution of 1mG.

ER 035M—Extremely accurate NMR magnetometer, 5mG from 450G to 20kG. Tracking rate, 1kG/3 sec. Optional EPR in-cavity probe.

Integrated solutions for Science and Industry

Let us tell you more

To get more information on these IBM Instruments products, just send the attached reply card or call 800-243-7054. In Connecticut, 800-952-1073. Or write IBM Instruments, Inc., Orchard Park, PO Box 332, Danbury, CT 06810. Outside the U.S.A. get in touch with your nearest Bruker-Spectrospin sales representative.
Automation makes it easy to use... Standard "extras" make it easier on the budget

New automation features and a new bit-slice multiprocessor combined with proven electronics make this FTNMR extraordinarily easy to use. And many features usually regarded as extras have been made standard equipment... so high performance capability doesn't have to mean high price.

Single-knob control
A single knob controls magnet and lock functions and a digital readout panel displays settings. Entering commands on the alphanumeric keyboard is simple and quick. Key functions such as shim, lock and receiver gain are automated. The Advanced Function FTNMR will perform complex experiments unattended for long periods.

Multiprocessor data system
The fast, micro-programmed, bit-slice CPU is supported by specialized processors that handle Fourier Transform, instrument control, data acquisition and output devices. This gives the instrument exceptional power and versatility, including multitasking capability.

Extras are standard
Features frequently costing extra, such as a broadband transmitter, digital plotter, diskette drive, hard disk drive and color display, are standard. And because of the economies that standardization brings, you get powerful performance at a modest price.

Let us tell you more
To learn more about the new Advanced Function Series FTNMR Spectrometers from IBM Instruments, send the attached reply card. Or call 800-243-7054. In Connecticut, 800-952-1073. Or write IBM Instruments, Inc., Orchard Park, PO Box 332, Danbury, CT 06810.

Integrated solutions for Science and Industry

IBM Instruments Inc.
July 1, 1985

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

Dear Barry:

Re: 27th Experimental NMR Conference

The 27th Experimental NMR Conference will be held at Baltimore, Maryland on April 13th through the 17th 1986 and will focus, as usual, on experimental aspects of nuclear magnetic resonance. The meeting will include both oral and poster presentations. The only mailing will be made in November of 1985 and will contain the registration information. Applications must be returned by January 15, 1986. This registration packet will include instructions for the submission of poster presentations. Any changes of address should be brought to the attention of P. Mark Henrichs, Eastman Kodak Company, Research Laboratories, Rochester, New York 14650, telephone 716-477-6229.

Very truly yours,

Robert G. Bryant
Dean's Professor

University of Illinois
at Urbana-Champaign

School of Chemical Sciences
505 South Mathews
Urbana
Illinois 61801

Wanted: Used 360/52 470 or 500/41 Magnets

I would be interested to hear if anyone has a used 360, 470 or 500/41 magnet for sale. Please contact me at the above address.

Eric Oldfield
Professor of Chemistry
June 21, 1985

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

"INADEQUATE Spectrum of A Novel Rearrangement Product from A Substituted Pyrrolidinone"

Dear Barry:

Fluorochloridone (I) is an active ingredient of RACER®, a registered selective herbicide from Stauffer Chemical Company. When (I) was reacted with sodium methoxide in methanol, a very unusual rearrangement product was isolated. Based on proton, carbon-NMR and mass spectra, the structure of this product was assigned as either II or III.

Only through the use of INADEQUATE technique, we were able to establish the actual connectivity of the pyrrolidinone ring and assign the structure of this product as (II) without ambiguity. The carbon chemical shifts and C-13 coupling constants of the pyrrolidinone ring are listed in Table I. The mechanism of this reaction and other spectroscopic data will be reported elsewhere.

Sincerely,

Lydia L. Chang

C. K. Tseng

mm:2:35
attachment
Table I*

<table>
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<tr>
<th>C#</th>
<th>δ (ppm)</th>
<th>J_C-C (Hz)</th>
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<tr>
<td>2</td>
<td>168.9</td>
<td>2 - 3 = 63.4, 2 - 5 = 9.8</td>
</tr>
<tr>
<td>3</td>
<td>125.3</td>
<td>2 - 3 = 63.5, 3 - 4 = 66.7</td>
</tr>
<tr>
<td>4</td>
<td>155.1</td>
<td>3 - 4 = 66.8, 4 - 5 = 42.1</td>
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<tr>
<td>5</td>
<td>89.5</td>
<td>4 - 5 = 42.1, 2 - 5 = 9.8</td>
</tr>
</tbody>
</table>

CONNECTIVITY: C₂ - C₃ - C₄ - C₅ - N - C₂

*The spectra were obtained on a Varian XL-200 NMR spectrometer. The INADEQUATE spectrum was obtained using C13SAT pulse sequence provided by Varian. The spectral width is 5KHz with 32K data points, pulse width (90°)=14 µsec, N=0 and JCC=54 Hz.
June 21, 1985

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

Dear Professor Shapiro:

Subject: CMR of Trifluoroacetanilide Derivatives

CMR chemical shifts and values for \( J_{CF} \) and \( J_{CCF} \) for several trifluoroacetanilide derivatives are reported here. All samples were dissolved in DMSO-\( d_6 \) and data were collected at ambient probe temperature. CMR data for trifluoroacetanilide are reported elsewhere (S. Bradamante and G. A. Pagan, J. Org. Chem., 45, 114 (1980)). A compilation of CMR substituent effects for monosubstituted benzenes (D. F. Ewing, Org. Mag. Res., 12, 499 (1979)) and the data for trifluoroacetanilide were used to test the reliability of calculated CMR chemical shifts for the aromatic ring carbons of the trifluoroacetanilide derivatives (Table I). Additivity parameters provided reliable CMR chemical shifts for the disubstituted compounds. The CMR chemical shifts calculated from the additivity parameters for the trisubstituted compound were not as useful because the experimental chemical shifts for the ring carbons of the trisubstituted compound are similar.

Yours very truly,

Douglas W. Lowman
Senior Research Chemist
Research Laboratories
P. O. Box 1972

bgm/TR0191f
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<th>Compound</th>
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</table>

*PPM relative to TMS

<sup>b</sup> in Hertz

<sup>c</sup> Number in parenthesis represents the difference in chemical shifts, i.e., 6(experimental)−6(calculated)
Professor Bernard L. SHAPIRO
Department of Chemistry
Texas A & M University
College Station, Texas 77843.

Re: Proton NMR measurements at different frequencies.

Dear Professor Shapiro,

The growing interest for biological applications of NMR is at the origin of the need for T1 and T2 measurements at different frequencies. We describe here the modification of a WP80SY wide bore Bruker spectrometer, modification which does not lose the advantage of the field-frequency lock.

As an example, the graph shows three Larmor lines for proton, phosphorus 31 and deuterium. The nominal value at 1.88 T are \( v_H = 80.4 \text{ MHz} \) and \( v_{lock} = 12.28 \text{ MHz} \) for deuterium. After reducing the field to about 0.71 T, the proton signal can be observed at 30.4 MHz with a broad band probe, whereas the electronic of the lock channel remains at 12.28 MHz. As it is shown on the graph, the lock can be achieved with a coaxial cell containing a phosphorus derivative. The same principle can be extended to other nuclei. The table shows a series of lock nuclei with the corresponding proton frequency.

Yours sincerely,

O. FABRE
Since its founding in 1960, Bruker has delivered many major contributions to the field of analytical instrumentation.

Here are some highlights:

1963: World's first commercial pulsed NMR spectrometer.
1967: World's first truly multinuclear high resolution NMR spectrometer.
1969: Introduction of Fourier transform techniques for NMR.
1974: Entrance into FTIR spectroscopy.
1983: Entrance into NMR imaging (MRI) and in-vivo spectroscopy.
1984: Introduction of fiber optics data link for high speed data transfer and ultra-fast array processors for FT applications in IR and NMR.

With this history of dedication to the needs of the analytical scientist behind it, Bruker today delivers a complete range of instrumentation, support, and services for GC/MS, HPLC, FTIR, ESR, and, of course, NMR.

NMR delivers answers to complex challenges of molecular structure determination in both liquids and solids. Only complete understanding of the physics and chemistry involved, and the manufacturer's total dedication to the development of appropriate instrumentation, can give you the analytical equipment you need to find those answers. And Bruker delivers.

Our philosophy is that your needs are to be supported at every turn, in every area. From hardware to software, from applications support to service and education, Bruker delivers there, too.

Hardware: Since our introduction of the world's first commercial pulsed NMR spectrometer in 1963, we have continuously advanced the frontiers of NMR tech-
ology. Today we offer an unequalled line of NMR spectrometer systems up to 500 MHz including such recent advances as in-vivo spectroscopy, mini- and whole body NMR imaging and real-time processing, such as the first fiberoptics data link for high-speed data transfer, and high speed array processors that perform Fourier transformations of 32 kiloword data tables in a few hundred milliseconds.

**Software:** In addition to providing the most advanced computer system for NMR and IR, we support you with user-friendly software packages for a wide variety of tasks far beyond routine acquisition and processing, such as two-dimensional NMR, complete system automation, reference data banks, and PASCAL compilers.

**Applications Support:** Our worldwide applications laboratories including those in Boston and Milton/Ontario have earned a reputation for being responsive to your requests, no matter how specialized or unusual. This commitment to support is an added value of Bruker instrumentation.

**Service:** We know how vital instrumentation availability is. That's why we have factory-trained service engineers in strategic locations, as close to you as possible. In the U.S., they are located in Billerica/MA, Mountain View/CA, Wilmington/DE, Chicago/IL and Houston/TX. And we offer maintenance contracts in addition to our basic full year warranty.

**Field Support:** Bruker actively fosters the exchange of ideas within the scientific community by sponsoring many international associations and local or national meetings, and by participating in most major symposia and exhibitions.

And our newsletter BRUKER REPORT keeps you abreast of technological developments.

If you have any questions about NMR, GC/MS, HPLC*, FTIR*, or ESR*, get in touch with us. Discover the many ways Bruker delivers.
Dear Professor Shapiro:

$^{53}$Cr and $^{17}$O Chemical Shift for Cr(VI) Species

As yet very little NMR data is available for the only magnetic isotope of chromium, $^{53}$Cr. One of the main reasons is the low sensitivity of the $^{53}$Cr nucleus which has a receptivity of $8.62 \times 10^{-5}$ relative to the proton (1). The natural abundance of $^{53}$Cr is only 9.55% and spin-spin coupling constants are expected to be small on account of the low magnetogyric ratio of chromium; a consequence of this is that it should be more advantageous to look for such couplings in the $^{53}$Cr spectra rather than in those of ligand nuclei. Another problem is that the nucleus is quadrupolar ($I = 3/2$). The reported values of the quadrupole moment, $Q$, range from 0.022 to 0.04 barn (2) and a more recent determination has measured $Q$ as $-0.15$ barn (3). Therefore quadrupolar broadening gives rise to a further decrease in signal-to-noise ratios. The only two $^{53}$Cr resonances so far reported for Cr in solution are for $\text{CrO}_4^{2-}$ and $\text{Cr(CO)}_6$ (4-6). The Cr nucleus is in a cubic environment in both of these species. The chemical shift of $\text{Cr(CO)}_6$ in THF is $-1795$ ppm relative to aqueous $\text{CrO}_4^{2-}$, which is taken as the standard.

Using a high field Bruker NMR spectrometer (WH 400) it has been possible to record $^{53}$Cr and $^{17}$O spectra for chromate, dichromate, halochromate and chromyl halide species. Tetraethylammonium salts of $\text{CrO}_4^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$ and $\text{CrO}_3X$ were prepared and spectra recorded for 1 molar solutions of acetonitrile. $\text{CrO}_3\text{X}_2$ species were recorded as melts; it was possible to reduce the linewidth of $\text{CrO}_2\text{F}_2$, which is known to be associated in the solid state, by using $\text{CClF}_2\text{CClF}_2$ as solvent. $\text{CrO}_2\text{ClF}$ was generated by halogen redistribution of $\text{CrO}_2\text{F}_2$ and $\text{CrO}_2\text{Cl}_2$. 

University of Nottingham
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MFAD/JS

5 July 1985

Professor B L Shapiro
Department of Chemistry
Texas A & M University
College Station
TX 77843
U.S.A.
The observed $^{53}$Cr and $^{17}$O chemical shifts and the approximate $^{53}$Cr linewidths are given in the Table.

The $^{53}$Cr chemical shifts recorded show that $^{53}$Cr exhibits inverse halogen dependence. When bonded to chlorine, chromium gives rise to a larger paramagnetic contribution than when fluorine is the ligand. This causes a deshielding effect, as can be seen in the series $\text{CrO}_2F_2$, $\text{CrO}_2ClF$ and $\text{CrO}_2Cl_2$. Thus, the chemical shift of $\text{CrO}_2Cl_2$ occurs to low field of $\text{CrO}_2F_2$; $\text{CrO}_2ClF$ has a chemical shift which is almost exactly the average of $\text{CrO}_2Cl_2$ and $\text{CrO}_2F_2$. Similar results have been obtained for the vanadyl species $\text{V}_2O_2Cl_2$, $\text{V}_2O_2ClF$ and $\text{V}_2O_2F_2$. (7).

In $\text{CrO}_3F^-$ a two bond oxygen-fluorine coupling constant, $^2J(^{17}O-^{19}F) = 33 $ Hz, was obtained from the $^{17}$O spectrum. However, no coupling was observed in $\text{CrO}_2F_2$ even when the $^{17}$O linewidth was reduced to 10 Hz by using CCl$_2$CClF$_2$ as solvent. We attribute this to the halogen scrambling process which is responsible for the facile production of $\text{CrO}_2ClF$ when $\text{CrO}_2Cl_2$ is added to $\text{CrO}_2F_2$. Incidentally, the integrals for the $^{53}$Cr spectra of such mixtures of $\text{CrO}_2F_2$, $\text{CrO}_2ClF$ and $\text{CrO}_2Cl_2$ indicates the equilibrium constant $K = [\text{CrO}_2ClF]/[\text{CrO}_2F_2][\text{CrO}_2Cl_2]$ to be 1.11. This value is slightly smaller than the value of 2, estimated by mass spectrometry (8) and significantly less than the value predicted for statistical halogen redistribution.

Yours sincerely

Eleanor Lloyd Jones
M F A Dove
Oliver Howarth

References
7. R.C. Hibbert, O. Howarth and N. Logan, in press.
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<thead>
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<th>CHEMICAL SHIFT (ppm)</th>
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</table>
Dr. B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas
U.S.A.

Dear Dr. Shapiro:

To initiate our subscription to the TAMU NMR newsletter, we describe how the 9.4 T magnet of our Bruker WM-400 NMR spectrometer is isolated from floor vibrations.

Since our research center was built directly over an underground train tunnel, detectors (our feet!) had forewarned us of severe floor vibrations. Prior to installation of the spectrometer, a survey of our building showed the presence of severe vibrations of 2.5 µm at 8-10 Hz, 2.18 µm at 6 Hz, and lesser ones at other frequencies. The Bruker specification for a 9.4 T magnet is that vibrations should not exceed 1 µm at any frequency. Due to the high sensitivity of the instrument, failure to eliminate the severe vibrations would result in symmetrical spikes/modulations at the base of strong resonances.

To isolate the magnet from the building vibrations we have mounted it on a Vibration Isolation Table (Figure 1) purchased from Optikon Corporation Ltd. They designed it based on the magnet's weight and center of mass, as well as the frequency and amplitude of the floor vibrations. From Figure 1, one sees that the magnet is inside the well of a cradle that floats ~ 2" above the floor. Vibration isolation of this cradle assembly is maintained by four automatic pneumatic isolator units (black bellows in Figure 1) mounted between the structural frame and the cradle assembly. The construction is...
entirely aluminum and needs only a ~ 20 psi air supply. The isolator units keep the base plate level and can quickly respond to, and compensate for any changes in the position of the cradle. The design is very effective at isolating the magnet from floor vibrations, even down to the low frequency vibrations which are usually difficult to remove. For example, the maximum displacements at 2 Hz and 4 Hz are 0.42 μm and 0.17 μm, respectively. The RMS amplitudes of the vibrations throughout the range of frequencies from 1 to 1000 Hz are all within the tolerances specified by Bruker.

We have found that this vibration isolation table does not pose any problems during probe and sample changes, probe tuning, or magnet shimming and maintenance. Another bonus of the vibration isolation table is that it restricts large objects (e.g. helium transfer dewars) from approaching within 1-2 feet of the magnet. The entire unit has been maintenance free for the 2 1/2 years that it has been in operation.

We recommend this or similar vibration isolation tables to anyone who does not have the luxury of a vibration-free floor for their superconducting magnet.

Yours very truly,

Gordon J. Kennedy
Research Chemist

R.S. Ozubko
Sr. Research Chemist

C.A. Michael
Technician

GJK/tlf

1472V

c.c. R. VanderLinden
Dear Professor Shapiro,

this letter hopefully saves us from your ultimatum. - For quite some time we have been active in the NMR spectroscopy of paramagnetic transitionmetal π-complexes. In the classical series of metallocenes there was a strange gap between chromium and iron. For instance, we were unable to obtain easily interpretable \( ^1H \) spectra at ambient temperature for several manganocenes with the general formula \((\text{Rcp})_2\text{Mn}\). This was strange since McConnell and Holm \(^1\) saw a signal for \(\text{Cp}_2\text{Mn} \) and Switzer, Wang, Rettig and Maki \(^2\) published data on \((\text{Mecp})_2\text{Mn}\). We then found out \(^3\) that at high temperature the full set of expected \( ^1H \) and even \(^{13}C \) signals appears. This led us to perform a more thorough investigation which showed that at low and high temperature the spectra are completely different. As shown in the figure no problems seem to arise at 390 K whereas two sets of \( ^1H \) signals are present at 200 K. One belongs to a species which has a low concentration (cf. insert A with the vertical scale blown up) and which can be related approximately to the signals at 390 K by the Curie law. The other set of signals is new; note that now the shifts are surprisingly small. The two sets of signals belong to two different spin isomers of the manganocene: \( ^2E_{2g} \) and \( ^6A_{1g} \). More precisely, the signals at 390 K have averaged shifts of about 85 % high-spin and 15 % low-spin species. Coales-
cence occurs near room temperature, and this is why serious
problems arise when detailed information is extracted under
these conditions as has been done in Ref. 2.

The low-spin/high-spin equilibrium can be nicely studied, e.g.
\[ \Delta H^\circ = 12 \text{ kJmol}^{-1}, \quad \Delta S^\circ = 45 \text{ Jmol}^{-1}K^{-1}, \quad \text{and} \quad \Delta G^\circ(6A_{1g} \rightarrow 2E_{2g}) \]
\[ = 47 \text{ kJmol}^{-1} \] in the case of (Mecp)$_2$Mn. It turns out that these
parameters depend strongly on the substitution of the cyclopentadienyl ligand. Together with some other influences on the
manganocene spin state a whole story results; it will be pub-
lished soon.

Yours sincerely

(F.H. Köhler) (N. Hebendanz)


NMR spectra of (Mecp)$_2$Mn dissolved in toluene-d$_8$ (S)
at 390 K (left) and 200 K (right).
Polarize \(^{13}\text{C}\) to \(^{103}\text{Rh}\) and reverse polarisation transfer.

Dear Barry,

In a cooperative work with Prof. JM LEHN and Dr JP KIN-TZINGER in Strasbourg, we had a look at the 50 \(^{103}\text{Rh}\) enriched \((\text{CO})_4\text{Rh}_2\text{Cl}_2\) compound.

The \(^{13}\text{C}\) spectrum shows the expected doublet \((J_{\text{C-Rh}} = 76 \text{ Hz})\) and we used a \({^{13}\text{C}}\text{Rh} \text{ INEPT}\) sequence to detect the \(^{103}\text{Rh}\) resonance (expected gain in sensitivity 7.9 / 1).

Much to our surprise, the \(^{103}\text{Rh}\) spectrum consists of two resonances \((\Delta \delta = 10.4 \text{ Hz with respectively 76 Hz and 152 Hz splittings})\).

This represents a nice determination of the enrichment procedure, and tells us that the Rhodium complex was enriched ca, 57 \% on both \text{CO}'s and 43 \% on only one \text{CO}. As a check, we run the \({^{13}\text{C}}\text{Rh} \text{ DEPT}\) experiment which provides the \text{Rh} - \text{2(CO)} resonance down (triplet) and \text{Rh} - \text{1(CO)} resonance up (doublet) (Fig 2). The \(\Delta \delta\) of -1, 096 ppm corresponds then to a \(^{12}\text{C}/^{13}\text{C}\) primary isotope shift on the Rhodium resonance.

Finally, figure 3 is the reverse \({^{103}\text{Rh}}\text{ Rh103} \text{ INEPT}\) (1) alternative for \text{Rh103} detection (measuring time : 1 hour).

With my best regards,

[Signature]

C. BREVARD

---

**Address:**

Société Anonyme au capital de 2.000.000 F régie par les Articles 118 à 150 de la loi sur les sociétés commerciales

Banque Populaire Wissembourg 17 607 00001 462 167 911 80 Rib 05 - CCP Strasbourg 19508 P - N° SIREN 311 020 911 00013
Fig 1: $^{13}$C Rh103 INEPT (lower: normal AQIT)
upper: INEPT AQIT

Fig 2: DEPT 135° $^{13}$C Rh103 INEPT Spectrum

Fig 3: 2D retro-INEPT [Rh103] $^{13}$C13 contour plot. Note the clean distinction between Rh-1C0 and Rh-2C0 species

1985 p. 65
Professor B. L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas 77843  
Re: Paramagnetic Radicals and Peptide Structure  

Dear Professor Shapiro:

Kopple and Schamper suggested several years ago that the $^1H$ NMR resonance line broadening produced by association with a nitroxide radical could be used to probe the amide protons in studies of peptide structure.(1) Recently we applied their method to study a monodisperse glutamate heptamer, Boc-(Glu-OMe)$_7$-0POE in CDCl$_3$, at conditions where we believe the molecule is free of intermolecular hydrogen bonding and molecularly disperse in solution. As Fig. 1 shows, addition of the radical preferentially broadens the Glu$_1$-Glu$_2$ NH protons in the N-terminus as opposed to the other NH groups in the C-terminal portion. By other criteria (coupling constant, temperature dependence, solvent denaturation), the N-terminal NH groups were implicated in intramolecular hydrogen bonding while NH groups in the C-terminal portion were solvent exposed. This gave a paradoxical situation wherein the NH groups most affected by the dipolar broadening (and presumably accessible to solvent as in the cyclic gramicidin S peptide(1)) were also the groups involved in hydrogen bonds.

A possible explanation was obtained through model building. Models show that in certain intramolecularly hydrogen-bonded forms, such as C$_7$ ring structures, the NH groups could be more accessible than NH groups in the extended conformation. The C$_7$ ring forced glutamate side chains to be equatorial, thereby permitting access of bulky free radical molecules to the hydrogen bonded NH. In addition, the C$_7$ rings are relatively planar and the radical has nearly equal access from either side of the plane. Seen in this light, the free radical results do not conflict with the other NMR data, and leads us to caution that criteria developed for cyclic peptides is not simply extrapolated to linear peptide systems.

Incidentally, monodisperse homo-oligopeptides show a surprisingly large fraction of intramolecular hydrogen bonding at dilute conditions in weakly interacting environments. For example, recent infra-red studies suggest...
that four NH groups are intramolecularly hydrogen bonded in a glutamate hexamer(2) and several years ago, we suggested that four NH groups are intramolecularly hydrogen bonded in a methionine heptamer in CDCl$_3$(3).

Sincerely yours,

Anthony A. Ribeiro

Dear Professor Shapiro,

PROTON SHIFTS AND S.C.S. IN SIMPLE MOLECULES

We have commenced an investigation in our laboratory into proton substituent chemical shifts (S.C.S.), in the pious hope that we may perhaps be able to quantitatively explain these shifts, in terms of the various mechanisms proposed previously.

We have, to date, been gathering data on molecules of precisely known geometry, and we selected the cyclic systems of norbornane, norbornene, adamantane and cyclohexane as suitable substrates. In the hope that our refined data may be of use to TAMU NMR readers I enclose a table of proton chemical shifts of the parent molecules and the S.C.S. of the bromo substituents in norbornane, adamantane, and cyclohexane.

Two comments may be pertinent. Every investigation we discovered in the literature of the low-temperature proton shifts of cyclohexane had used CS$_2$ as solvent. This well-known anisotropic solvent produces large differential solute shifts, as can be seen by comparison with the date for CFC$_3$ solvent which we obtained.

Finally, no combination of the usual effects attributed to the bromo substituent can even begin to explain quantitatively the data in the Table.

With best wishes,

Yours sincerely,

DR. R.J. ABRAHAM


Substituent chemical shift for bromo compounds

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This work: Previous Data

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New values for $Q(^6\text{Li})$, $Q(^7\text{Li})$ and $Q(^{14}\text{N})$ from quantum chemistry

Dear Professor Shapiro,

We have recently developed an improved method for calculating electric field gradients, $q$, in diatomic molecules by combining a two-dimensional ("2D"), fully numerical Hartree-Fock value with correlation and rovibrational contributions obtained from Complete Active Space (CAS SCF) LCAO calculations using large basis sets. The 2D method provides for the first time an unequivocal Hartree-Fock limit for $q$ while the CAS SCF method accounts for most of the correlation. The final values are given in the Table.

Concerning $^7\text{Li}$, the old LiH value of Green suffers from basis-set problems. His $q_{\text{HE}} (R = 3.015 \text{ a.u.})$ is $-0.044 \text{ a.u.}$ while our benchmark is $-0.0398 \text{ a.u.}$. The two atomic measurements have large experimental error bars. Of the nuclear, Coulomb scattering values, that of ref. 7 agrees with our value while that of ref. 6 does not.

In the case of $^{14}\text{N}$, the old small-basis values from polyatomic molecules without correlation ($Q(^{14}\text{N}) = 0.016 \text{ b}$) are inadequate. Our solid-state $N_2$ and gas-phase $NO^+$ values are in an adequate agreement with each other and with the atomic, $N^+ 2p3p \, ^1P_1$ value of Winter and Andrä.

Please credit this letter to the account of Professor Kalevi Pihlaja at the University of Turku.

Sincerely yours,

Pekka Pyykö
Professor of Chemistry
References


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<th>System</th>
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Table 1. Values of nuclear quadrupole moments $Q$ (in barn = $10^{-28}$ m$^2$)

Prof. B. L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station, Texas 77843-3255, U.S.A.

Selenium-77 MAS NMR of Inorganic Compounds

Dear Barry:

In collaboration with Gary Schrobilgen and Mar Bjorgvinsson of McMaster University I have been exploring possible uses of solid-state high-resolution selenium-77 nmr in inorganic chemistry and report some preliminary results. Selenium-77 is an easy nucleus for MAS nmr in that it is spin-1/2 and 7.6% abundant, but long relaxation times can be a problem. Relaxation delays of 5 minutes between 30° pulses seem optimal for some samples. A further problem is large chemical shift anisotropy that can lead to multiple spinning sidebands when the symmetry about selenium is low. This effect is illustrated in the attached spectra of selenium dioxide.

Na₂SeO₄ has tetrahedral symmetry about selenium and K₂Se has the antifluorite structure with eight potassium atoms about selenium at the vertices of a cube. Each of these compounds gives a single peak with negligible spinning sidebands, at +1037 and -442 ppm from Me₂Se, respectively. SeO₂₃, in contrast, has a low-symmetry structure involving infinite chains in which selenium is bonded to three oxygens in a flat pyramid; two of the oxygens are bridging and one is terminal. At both 4.7 tesla (spectrum A) and 9.4 tesla (spectrum B) a multiple-sideband pattern is obtained. Variable spin rate experiments identify the centre band at +1462 ppm from Me₂Se.

Thus selenium-77 MAS nmr seems easy until the more interesting (i.e., less symmetrical) compounds are tried. Recently-developed sideband suppression methods should however get around this problem. The spectra shown were obtained on the Bruker CXP-200 and WH-400 instruments of the South Western Ontario High Field Nmr Centre, with the assistance of Bob Lenkinski and Bill Klimstra.

I hope this contribution suffices to reinstate the Brock University subscription.

Yours sincerely,

J. S. Hartman,
Professor of Chemistry.
$^{77}$Se MAS NMR Spectra of SeO$_2$.

A. 38.2 MHz, 43 scans, 5 min relaxation delay between 30° pulses, 100 Hz line broadening.

B. 76.3 MHz, 14 scans, 5 min relaxation delay between 30° pulses, 50 Hz line broadening. Some sidebands are folded.

**NMR Spectroscopist**

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This position is being offered by the Scientific Services Department of the Chemical Research Division of American Cyanamid located in Stamford, Connecticut. As a member of this department, the candidate will join more than 90 other scientists who utilize a complete range of modern analytical tools to promote the growth of Cyanamid's chemical businesses. As a corporate resource for analytical excellence in a number of key areas, including analytical microscopy, inorganic analysis, polymer chemistry, physical chemistry and testing, and industrial hygiene, we actively participate in research, production, and customer service projects in Cyanamid's other business areas: medical, agricultural, and consumer products.

We offer a competitive salary and benefits package. Cyanamid is an equal opportunity employer. Those interested in further consideration should forward a resume to Dr. Teresa L. Muchnick, Group Leader, Chromatography and Spectroscopy, American Cyanamid, 1937 West Main Street, P.O. Box 60, Stamford, Connecticut.
Dear Professor Shapiro,

Intramolecular Interactions of the Methyl Group

As part of our continuing effort to study the above interaction we have measured the spin-lattice relaxation parameters of 3-heptyne (ethyl-n-propylacetylene) in the neat liquid at 28°C and 25.05 MHz:

\[
\begin{array}{cccc}
\text{C} & - & \text{C} & - & \text{H}_2\text{C} & - & \text{C} & - & \text{C} \\
T_1/\mu s & 8.7 & 15.5 & 12.6 & 10.4 & 10.7 \\
\eta & 1.9 & 1.8 & 2.0 & 1.9 & 1.7
\end{array}
\]

The methyl carbon of the ethyl group has substantially reduced \(T_1\) value and this may indicate that the internal rotation of this methyl group is hindered so that the contribution to nuclear relaxation from the dipole-dipole mechanism is increased. The unusually high NOE factor (\(\eta\)) for this methyl carbon is consistent with this explanation. The methyl group is oriented at a favorable angle with respect to the triple bonds, so that an electrostatic (attractive) interaction between the polarizable methyl hydrogens and the \(\pi\) electron system can take place, thereby reducing the rate of rotation of the methyl group. The methyl carbon of the ethyl group in 3-heptyne is part of a three-carbon chain attached to a \(\pi\) system and the observation of a reduced \(T_1\) value is similar to that of the methyl carbon of the \(n\)-propyl group attached to an electronegative atom, oxygen or nitrogen (1).

The methyl carbon of the \(n\)-propyl group in 3-heptyne does not show a significantly reduced \(T_1\) value, no doubt because it is part of a four-carbon chain in which the freedom of rotation about an extra C-C bond does not favor the weak attraction between the methyl hydrogens and the \(\pi\) electron system.

Yours sincerely,

(1) S. Ng, Org. Magn. Reson. 21, 50 (1983)
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Dear Barry:

Your readers may be interested in the following meeting.

U.S.-Latin American Workshop on Recent Developments in Organic and Bioorganic NMR, with emphasis on research in developing countries, will be held July 7-11, 1986, in Campinas, Brazil. This Workshop follows immediately the ISMAR conference in Rio de Janeiro. The Workshop will cover current developments and will explore how scientists in developing countries can gain access to new NMR methods for use in their research. The tentative list of speakers includes M. Barfield, A. A. Bothner-By, E. L. Eliel, J. B. Grutzner, J. B. Lambert, E. P. Mazzola, D. E. Wemmer, C. S. Yannoni (U.S.A.), F. Y. Fujiwara, A. J. Marsaioli, M. A. P. Martins, R. Rittner, P. R. Seidl, J. A. Vanin, N. Zanatta (Brazil), R. H. Contreras, D. G. de Kowalewski, V. J. Kowalewski (Argentina), and P. Laszlo (Belgium). For further information please contact one of the Directors.

Professor Joseph B. Lambert
Northwestern University
Department of Chemistry
2145 Sheridan Road
Evanston, IL 60201
U.S.A.

Professor Roberto Rittner
Instituto de Quimica
Unicamp
Caixa Postal 6154
13083 Campinas--SP
Brazil

Sincerely,

Joseph B. Lambert

JBL:cs
Professor Bernard Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas 77843

POSITION AVAILABLE - NMR SPECTROSCOPIST

June 20, 1985

Dear Professor Shapiro:

Procter & Gamble Company has an immediate entry-level staff opening in NMR spectroscopy at the Miami Valley Laboratories in Cincinnati, Ohio. Applicants should have a Ph.D. in chemistry, biochemistry or a related field, preferably with postdoctoral experience. A strong background in high-field multinuclear FT-NMR and experience with two-dimensional NMR techniques are essential. Applicants should have the ability to solve chemical and structural problems using NMR spectroscopy, have a demonstrated interest in biochemical problems, and be knowledgeable with computer interfacing. Our primary interest is the study of the structure and dynamics of biomolecules in solution. The NMR laboratory is currently equipped with a Bruker CXP-300, JEOL FX-270 and several low-field spectrometers. We will be taking delivery of a General Electric GN-500 by August.

Candidates must be U.S. citizens or hold a permanent resident visa and should send their resumes to:

Dr. T. J. Logan, Manager  
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Sincerely,

Fouad S. Ezra

Corporate Research Division
July 16, 1985

Dr. Barry Shapiro
TAMU NMR Newsletter
Texas A&M University
Department of Chemistry
College Station, Texas 77843

Dear Dr. Shapiro:

Union Carbide has an immediate opening for an NMR spectroscopist at our Bound Brook Technical Center located in central New Jersey. The position is in the NMR laboratory of the R&D Analytical Section. This laboratory currently is equipped with an IBM WP-200/SY with a C-13 CPMAS accessory, an IBM WP-270/SY, and a Varian CFT-20. An IBMBruker AM-360 is expected to be delivered in October of this year.

The successful applicant should have a Ph.D. degree in chemistry with experience in high resolution, high field multinuclear NMR. Experience in polymer analysis and 2-D, multipulse, and solid state NMR would also be helpful. The assignment involves co-responsibility for operation of the NMR laboratory and requires extensive interaction with other members of the technical staff. The focus of the NMR laboratory is on the structure elucidation of polymers and polymer-related materials.

Interested applicants should send their resume to DR. K. POLLAK - UNION CARBIDE CORPORATION, P.O. BOX 670, BOUND BROOK, NJ 08805. Salary and benefits are competitive and commensurate with qualifications and experience. Union Carbide Corporation is an equal opportunity employer.

Sincerely,

K. Pollak

/rp
August 1, 1985

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

Re: Postdoctoral Position

Dear Barry:

I would like to announce a postdoctoral opening in my laboratory at the Cancer Center. The work will involve the structural studies of DNA oligomers and small proteins using various NMR techniques including 2D-NMR methods. Prior experience in this area and/or computer programming (Fortran and Basic) would be a definite advantage. An additional postdoctoral position involving in vivo applications of NMR may become available in the near future. The facilities at the Cancer Center include two high-field superconducting NMR spectrometers (Bruker WH-400 and CXP-300/200) and an iron magnet system (HX-90). Interested candidates should send a resume and arrange for three letters of recommendation to reach me at the Cancer Center.

Yours sincerely,

N.R. Krishna, Ph.D.  
Associate Professor of Biochemistry  
Director, NMR Core Facility
Dear Dr Shapiro,

We have recently studied quinuclidine, 1, in various hydrogen bond donors [1]. We found, by carbon-13 relaxation measurements, that the hydrogen bond formation led to substantial anisotropy in the rotational diffusion of quinuclidine. As the inert "reference" solvent, we have in that work used benzene. It bothered us, however, that even in this solvent the anisotropy was by no means negligible, the ratio of the diffusion constants $R_{\text{parallel}}/R_{\text{perpendicular}}$ being about 2.5. Recently, we took another look at the problem by studying the motion of 1 in mixtures of benzene and cyclohexane. The results are shown in Figure 1. In pure cyclohexane, quinuclidine reorients almost isotropically and the anisotropy increases quickly upon adding benzene. Obviously, the data indicate that the presence of benzene hinders the reorientation of the symmetry axis of quinuclidine due to some kind of attractive potential. An interesting question to ask is which geometrical arrangement of the two molecules gives such a potential minimum. We are going to try to look into this problem in the near future.

Yours sincerely

Jozef Kowalewski
Arnold Maliniak

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