TEXAS A&M UNIVERSITY
NMR NEWSLETTER

No. 426
March 1994

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TABLE 1 DEUTERATED SOLVENTS

Cat. No.	Description	Formula	Min. Iso. (Atom %D)	Density (g/ml)	MP (°C)	BP (°C)	$-\chi_v \times 10^6$ @ (°C)
D-11	Acetone-d_6	CD_3COCD_3	99.9%	1.12	-94	56	0.551 (32)
D-120	Acetone-d_6 + TMS	CD_3COCD_3	99.9%	0.87	-94	56	
D-13	Acetone-d_6	CD_3COCD_3	99.9%				0.460 (20)
D-121	Aceonte-d_6 + 1% TMS		99.8%				
D-129							
D-14							0.643 (20)
D-21							0.611
D-122							
D-130							
D-28	Chloroform-d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
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WCV-XL (XL-100)	11" X 26"	XL-100 (and FT)	Gridded-Two Color
WCV-XLFT-100	11" X 26"	XL-100 (and FT)	Gridded-Two Color
WCV-XL-200	11" X 26"	XL-200, XL-300, XL-400	Gridded-Two Color
WCV-20 (CFT-20)	11" X 16 3/4" X 17"	CFT-20, FT-80, FT-80A All Models 11" X 16 1/2" or 16	Gridded-Two Color Blank

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FORTHCOMING NMR MEETINGS

Symposium on *In Vivo* Magnetic Resonance Spectroscopy VII, Monterey, California, **April 9 - 10, 1994**; Contact: Radiology Postgraduate Education; Room C-324, University of California School of Medicine, San Francisco, CA 94143-0628; Phone: (415) 476-5731; Fax: (415) 476-9213; For registration, call (415) 476-5808; Fax: (415) 476-0318 See TAMU NMR Newsletter 422, 47.

35th ENC (Experimental NMR Conference), Asilomar Conference Center, Pacific Grove, California, **April 10 - 15, 1994**; Contact: ENC, 815 Don Gaspar, Santa Fe, NM 87501; (505) 989-4573; Fax: (505) 989-1073 See TAMU NMR Newsletter 422, 9.

25th New Mexico Regional NMR Meeting (otherwise known as the $(NMR)^2$ Meeting), Albuquerque, New Mexico, **April 16, 1994**; Contact: Eiichi Fukushima at (505) 262-7155; Fax: (505) 262-7043.

Gordon Conference on Magnetic Resonance in Biology and Medicine, New England College, Henniker, NH, **July 17 - 22, 1994**; Contact: Dr. Carlyle B. Storm, Director, Gordon Research Conferences, Gordon Research Center; Univ. of Rhode Island, Kingston, RI 02881-0801; Tel. (401) 783-4011 or -3372; Fax: (401) 783-7644.

8th International Symposium on Molecular Recognition and Inclusion, Ottawa, Ontario, Canada, **July 31 - August 5, 1994**; Contact: H. Morin-Dumais, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, ON K1A 0R6, Canada; (613) 993-1212; Fax: (613) 954-5242 See TAMU NMR Newsletter 419 34

Solid-State NMR Symposium, 36th Rocky Mountain Conference on Analytical Spectroscopy, Denver, CO, **July 31 - August 5, 1994**; Contact: R. E. Botto, Chemistry Divn., Argonne Natl. Lab., Argonne, IL 60439; (708) 522-3524; Fax: (708) 252-92882 See TAMU NMR Newsletter 424, 46.

2nd Meeting, Society of Magnetic Resonance, San Francisco, California, **August 6 - 12, 1994**; Contact: SMR Berkeley Office, 1918 University Ave., Suite 3C, Berkeley, CA 94704; Tel. (510) 841-1899; Fax: (510) 841-2340.

Gordon Conference on Order/Disorder in Solids, New London, New Hampshire, **August 7 - 12, 1994**; Contact: Prof. M. A. White, Dept. of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3; Tel. (902) 484-3894; Fax: (902) 494-1310. See TAMU NMR Newsletter 421, 44.

Continued on page 45

ETH Eidgenössische Technische Hochschule Zürich
Ecole polytechnique fédérale de Zurich
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Swiss Federal Institute of Technology Zurich

Laboratorium für Anorganische Chemie
Prof. Dr. Paul S. Pregosin

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Universitätstr. 6
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CH-8092 Zürich

Prof. Barry Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto CA 94303
USA

Feb. 10 ,1994
(received 2/15/94)

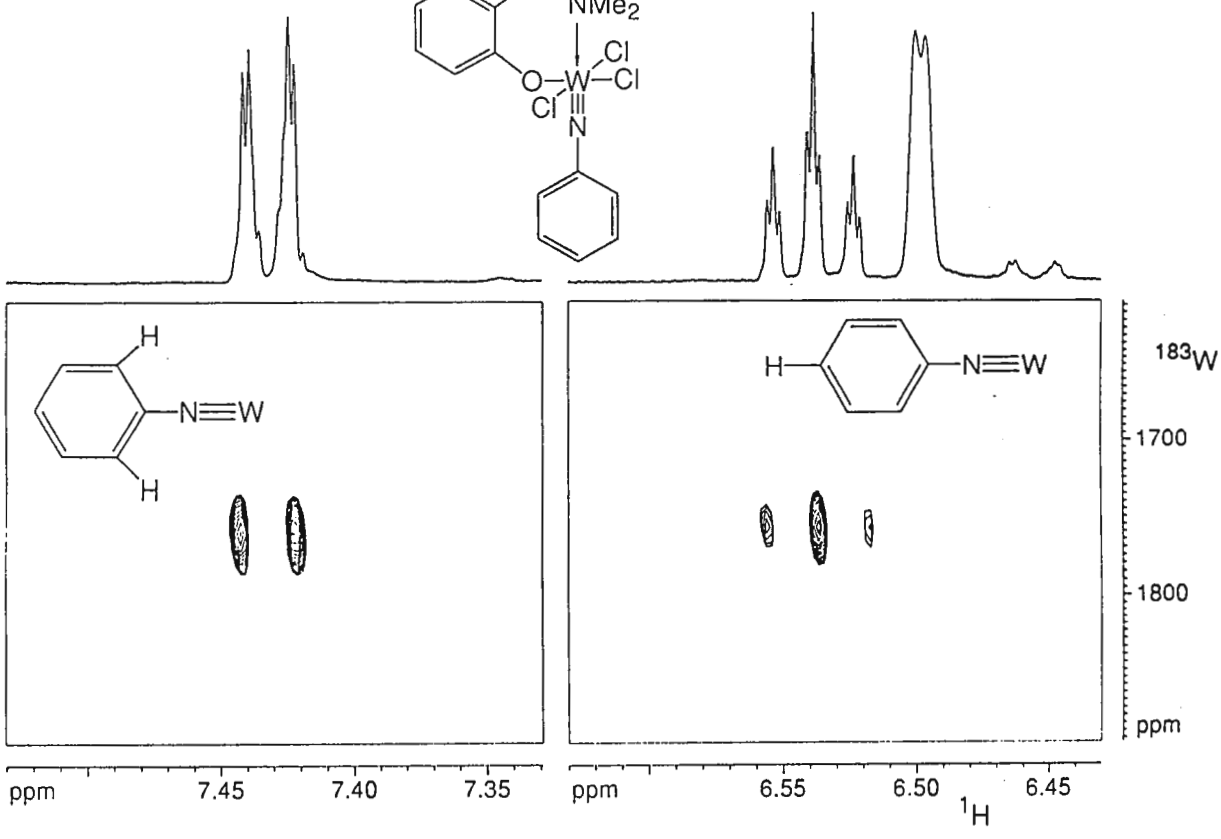
Dear Barry

There is an increasing interest in imido complexes due to their possible involvement in homogeneous metathesis chemistry. Since tungsten is one of the metals capable of this reaction, we have begun a study of the ^{183}W NMR characteristics of such complexes. Shown below is the HMQC ^{183}W inverse spectrum for the complex shown. Interestingly, we can use the long-range coupling to the *ortho* and *para* protons of the NPh ligand to detect the metal. This is general for this class of complexes even though these couplings are ca. 0.7 and 0.3 Hz, respectively. A detailed report will appear shortly in MRC.

Sincerely

Paul

Prof. P.S. Pregosin



750 MHz NMR SPECTROSCOPY AT BRUKER

RESULTS IN THE FIRST YEAR

STABILITY AND HOMOGENEITY

The Bruker 750 MHz magnet, which was developed in collaboration with the Nuclear Research Center in Karlsruhe, utilizes a very conservative cooled superstabilized magnet design, which represents unique innovation and a breakthrough in high-field high-resolution NMR. This superstabilized design offers more than "just 150 MHz more", by providing unprecedented low drift and short-term stability not previously available from any other magnet design.

After initial energization, we reported long-term drift of less than 3 Hz/hr. Recently unlocked, uncompensated drift tests, however, indicate a barely measurable **drift of less than 0.3 Hz/hr**. Equally important to modern NMR spectroscopy **is short term stability**, which for the entire system can be nicely measured with the well-known spin-echo difference (SED) test. An SED experiment (not shown) on chloroform was performed on an AMX750 equipped with a Digital Lock™. The suppressed centerband of 20 experiments (2 scans, 1 Hz line broadening) was well below 50% of the satellite height, indicating extremely good short-term systems and magnet stability.

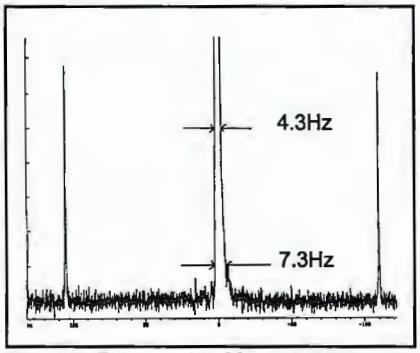


Figure 1: 5 mm probe, Non-spinning lineshape

The Bruker 750 magnet was designed with the largest homogeneous region of any 54 mm magnet which we have ever built, in order to obtain optimal resolution and lineshape for 5 mm samples, but also for optimal results on 8 mm water-suppression probes. Figure 1 demonstrates a **non-spinning lineshape** on 1% chloroform **of 4.3 over 7.3 Hz,** using a BOSS™2 shim system.

Figure 2 shows the standard 5% ODCB resolution test, with a measured **resolution of 0.20 Hz**. We are pleased to report that in terms of ease of use the 750 MHz system is in fact particularly well-behaved and easy to shim due to its excellent homogeneity.

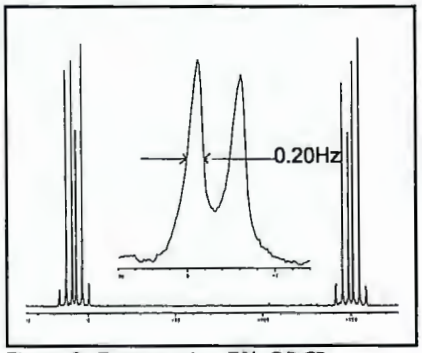
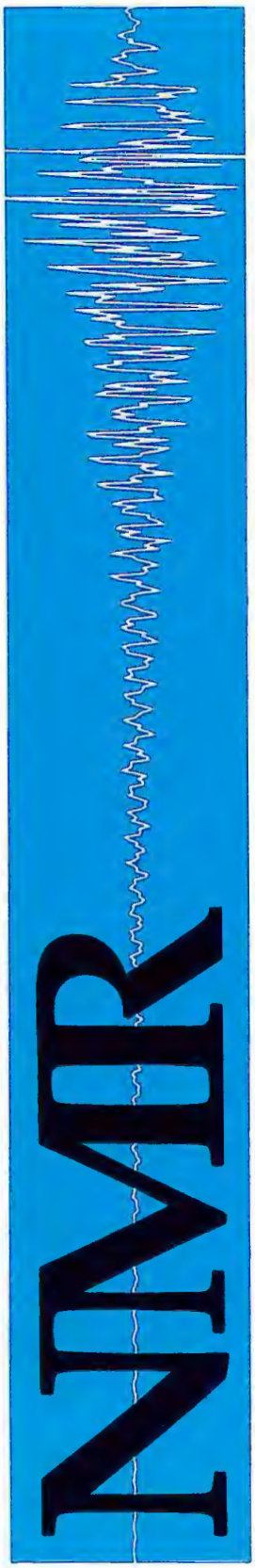


Figure 2: 5 mm probe, 5% ODCB resolution test



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NMR

SENSITIVITY AND BANDWIDTH

Initially, 750 MHz sensitivity measurements on 0.1% EB were only in the 800-900:1 range, because essentially 600 MHz technology was extrapolated to 750 MHz. In recent months, entirely new probe and rf technology was introduced which was designed specifically for high proton sensitivity, as well as for short ^{13}C 90° pulse width to cover the large bandwidth of carbon on a 750 MHz spectrometer.

Here we would like to report a 0.1% EB sensitivity measurement using a new-style 5 mm ^{1}H-selective probe with S/N = **1,245:1** (spinning), shown in Figure 3. A 13.5 hour NOESY of 0.3 mM lysozyme in 90%H_2O/10%D_2O, acquired on a TXI triple resonance probe is shown in Figure 4.

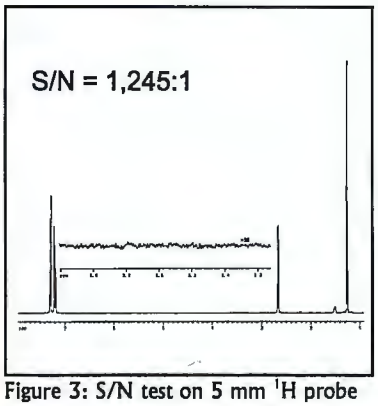


Figure 3: S/N test on 5 mm ^{1}H probe

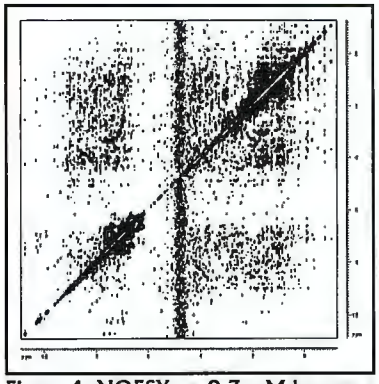


Figure 4: NOESY on 0.3 mM lysozyme

Even more interesting for most NMR experiments on labeled peptides, protein or nucleic acids is the high S/N of **1,150:1** (spinning) and **1,075:1** (non-spinning) for a new-style triple-resonance GRASP II TXI™ 5 mm probe equipped with a shielded z-gradient, as shown in Figure 5a and b.

A sensitivity test which is more comparable to modern biological experiments is the measurement of the S/N of the anomeric protons of sucrose in 90%H_2O/10%D_2O. On a 750 MHz GRASP II TXI we have measured the S/N of the anomeric proton at 260:1 without salt; with 400 mM salt concentration we still obtain 197:1, and even with 1 M salt concentration, the S/N is 178:1.

The new style GRASP II TXI probe offers very high ^{13}C bandwidth, and has **a measured 90° pulse width of only 10.5 microsec.**

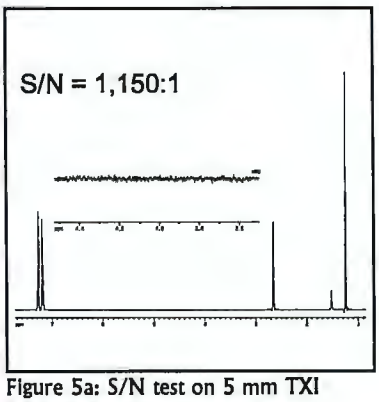


Figure 5a: S/N test on 5 mm TXI GRASP II probe, spinning

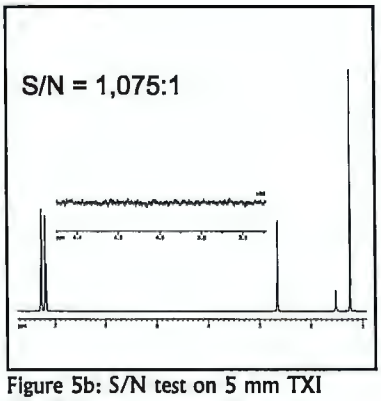


Figure 5b: S/N test on 5 mm TXI GRASP II probe, non-spinning

BRUKER

DISPERSION AND SELECTIVE EXCITATION

The greater spectral dispersion which is inherently available at 750 MHz can often significantly reduce peak overlap, and therefore also affords unique opportunities for selective excitation of resolved spectral features. Figure 6 illustrates the higher dispersion available at 750 MHz with an inverse correlation spectrum of human plasma: many important signals which overlap or partially overlap even at 600 MHz are nicely separated at 750 MHz.

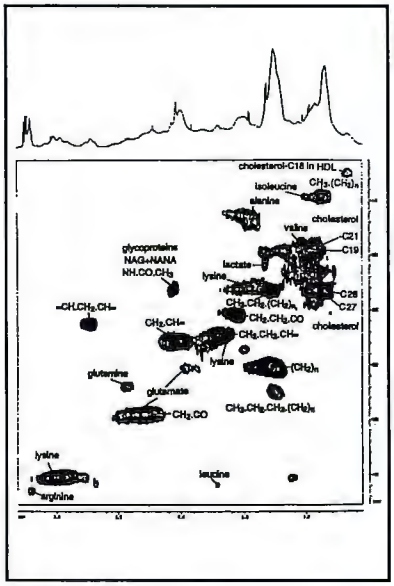


Figure 6: Inverse correlation of human plasma

3D NMR SPECTROSCOPY

At ENC 1993 we showed a series of demanding 3D experiments including **NOESY-TOCSY**, **HNCO**, **HN(CO)CA** (Figure 8) using 5 mm selective and TXI probes. Here we wish to report 750 data on a demanding new 3D cross polarization experiment, called **HEHOHEHAHA**. Figure 7 shows a 2D slice from this experiment on ^{13}C-labeled sucrose measured with a 5 mm GRASP II TXI probe.

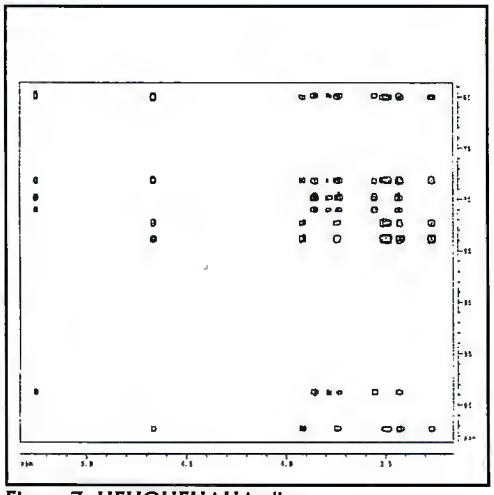


Figure 7: HEHOHEHAHA slice

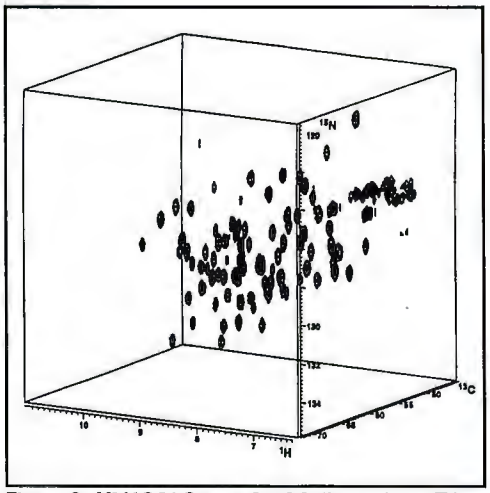
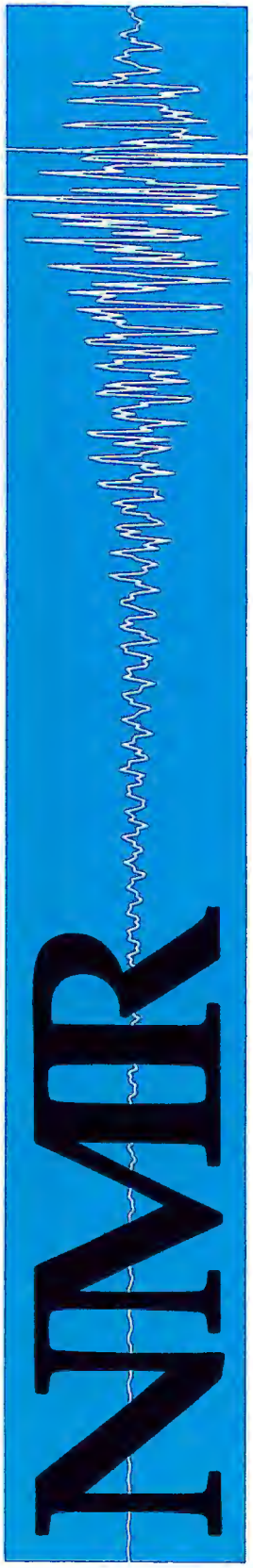


Figure 8: HN(CO)CA on 2 mM ribonuclease T1



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NMR

GRADIENT SPECTROSCOPY

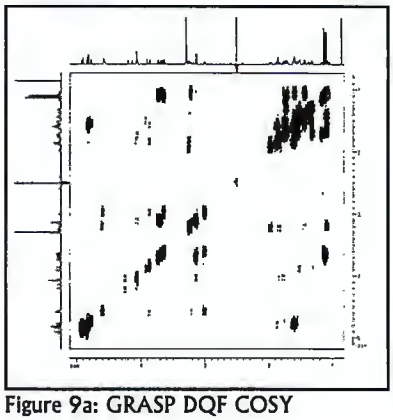

Figure 9a: GRASP DQF COSY

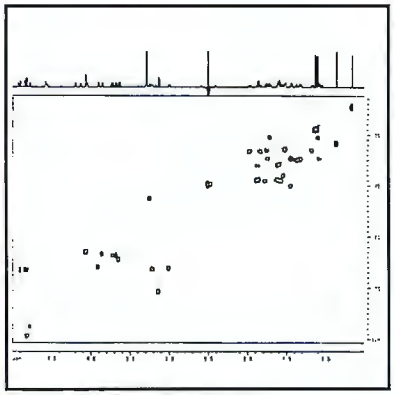

Figure 9b: GRASP HSQC

Various GRAdient SPectroscopy (GRASP™) probes are available now at 750 MHz. Most 5 mm probes are available as either **GRASP II** (shielded z-gradient) or **GRASP III** (shielded x,y,z gradients). The new 2.5 mm TXI microprobe is available as a GRASP II probe. A radiofrequency homonuclear gradient spectroscopy (**rf-GRASP**) 5 mm probe is now available at 750 MHz as well. Upon request, most 8 mm probes can be equipped with GRASP II.

The GRASP results reported here were all acquired on a 5 mm GRASP II TXI probe. Figure 9a shows a GRASP DQF COSY of digoxin in DMSO-d6. Figure 9b shows a natural abundance HSQC experiment on the same sample with 4 scans and 128 increments. Finally, Figure 10 shows a gradient ^{15}N-HSQC without presaturation of 2 mM doubly-labeled RNASE in 90%H_2O with a total acquisition time of 14 minutes.

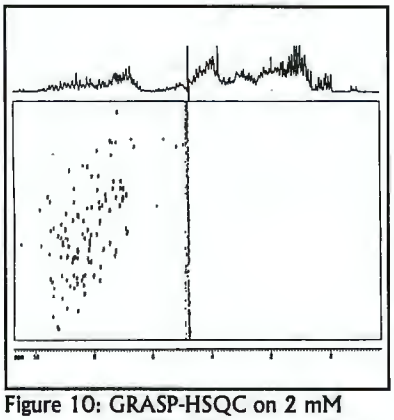

Figure 10: GRASP-HSQC on 2 mM doubly-labeled RNASE in water without presaturation

SOLID-STATE SPECTROSCOPY

Figure 11 shows 750 (upper trace) and 500 MHz (lower trace) MAS spectra at 15 kHz spinning speed.

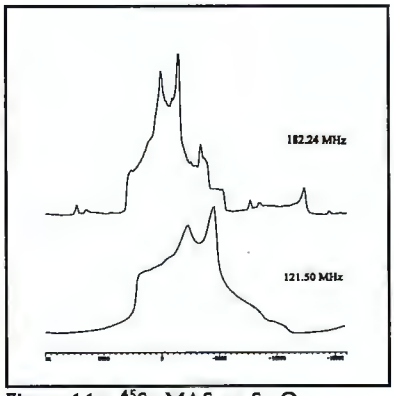

Figure 11a: ^{45}Sc MAS on Sc_2O_3

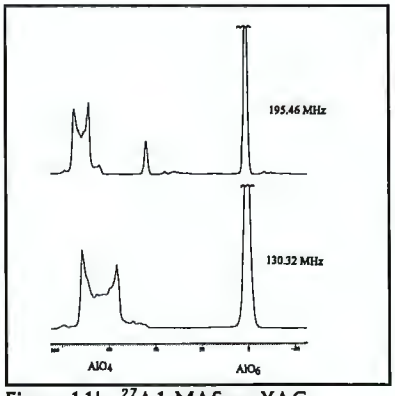

Figure 11b: ^{27}Al MAS on YAG

Determination of CH, CH_2 and CH_3 Resonances of Drug-DNA Complexes by E-HMQC Experiments

Dear Dr. Shapiro:

Identifying CH, CH_2, and CH_3 is particularly useful in the resonance assignment of large molecules, especially nucleic acids and proteins. One of effective approaches is to employ multiplicity editable heteronuclear correlation experiments (1-3). These experiments take advantage of both multiplicity editing and heteronuclear correlation techniques. The multiplicity editing technique provides information to identify CH, CH_2, and CH_3 resonances. On the other hand, heteronuclear correlation experiments provide substantial spectral resolution to resolve proton resonances through the large ^{13}C chemical shift dispersion.

Complete assignment of proton resonances is essential and important for structural determination of DNA and its complexes. Generally, proton resonance assignments for DNA can be readily made by homonuclear 2D NMR experiments except for 4' and 5'/5" sugar protons. The difficulty in 4' and 5'/5" proton resonance assignment lies in the fact that non-terminal 4' and 5'/5" proton resonances are often overlapped in a narrow spectral region between 4.0 and 4.5 ppm. It is worth noting that the sugar 4' CH and 5' CH_2 resonances have different multiplicities. Thus editable heteronuclear correlation experiments can be applied to identify these protons. Considering that uniform ^{13}C isotopic labeling is difficult in the case of nucleic acids, the experiments have been designed to be applicable to natural abundance samples.

Here we demonstrate the feasibility of the editable heteronuclear multiple quantum correlation experiments (E-HMQC) for nucleic acids at natural abundance. We have successfully applied these experiments to several DNA systems, including a nogalamycin$_2$-d(AGCATGCT)$_2$ complex and a luzopeptin-d(CATG)$_2$ complex of which the 3D structures have been determined (4,5). We chose the nogalamycin$_2$-d(AGCATGCT)$_2$ complex as an example to illustrate the application to nucleic acids.

Generally, identification of CH, CH_2, and CH_3 requires three E-HMQC spectra with different β flip angles (1, 3). However, in the case of nucleic acids, CH_3 resonances can be readily identified by their characteristic spectral features, such as, upfield chemical shift and strong intensity. The E-HMQC spectrum with the β flip angle of 0° shows opposite sign for the CH_2 resonances with respect to the CH and CH_3 resonances (2). Therefore, this single spectrum is usually sufficient to identify the CH, CH_2, and CH_3 resonances. Figure 1 shows three pulse schemes of the E-HMQC experiment for this purpose. The pulse scheme (a) is the original form we proposed previously (2). This scheme provides a very good suppression for undesired ^{12}C-bonded proton signal to yield low t_1 noise in the spectra. After the 90°(^1H) - $1/4J_{CH}$ - 180°(^1H, ^{13}C) - $1/4J_{CH}$ - 90°(^1H) pulse sandwich, ^1H-^{13}C coherence is in the form of longitudinal spin order, while ^{12}C-bonded proton magnetization remains in the single quantum state in the x-y plane. The undesired signal from the ^{12}C-bonded protons is then destroyed by a field gradient pulse (6). Scheme (b) is a modified form of scheme (a). This scheme utilizes the technique of flipping ^{12}C-bonded proton magnetization back to the z axis (7) to improve dynamic range. It does not require the field gradient hardware, and avoids potential instability caused by applying the field gradient pulse. In the case of differentiating CH from CH_2 groups, the double refocus pulse pairs, - $1/4J_{CH}$ - 180°(^1H, ^{13}C) - $1/2J_{CH}$ - 180°((^1H, ^{13}C) - $1/4J_{CH}$ - in scheme (b) can be replaced by a single refocus pulse pair, - $1/2J_{CH}$ - 180°(^1H, ^{13}C) - $1/2J_{CH}$ - . This modification leads to a simplified form, scheme (c), with fewer pulses.

Figure 2 shows a ^1H- ^{13}C E-HMQC spectrum of nogalamycin$_2$-d(AGCATGCT)$_2$ complex acquired by the pulse scheme (c). The spectrum shows negative peaks for sugar 2' and 5' CH_2 groups but positive peaks for other CH and CH_3 groups. Assignments for the 1' CH, 2' CH_2 and 3' CH resonances can readily be made in the ^1H- ^{13}C correlation spectrum since the sugar 1'-3' proton resonances have been assigned by homonuclear experiments (4). On the other hand, the 4' CH and 5' CH_2 can be identified since they show opposite signs in the E-HMQC spectrum. The detailed resonance assignment will be described elsewhere (Zhang, unpublished results).

Acknowledgment:

The authors would like to thank Professor Dinshaw J. Patel for his kind support. This work made use of the National Magnetic Resonance Facility at Madison.

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6. D. Bruhwiler and G. Wagner, J. Magn. Reson., 69, 546 (1986).
7. L. Müller, J. Am. Chem. Soc., 101, 4481 (1979).

Please credit this contribution to the account of Dr. Nina C. Gonnella.

(received 2/17/94)

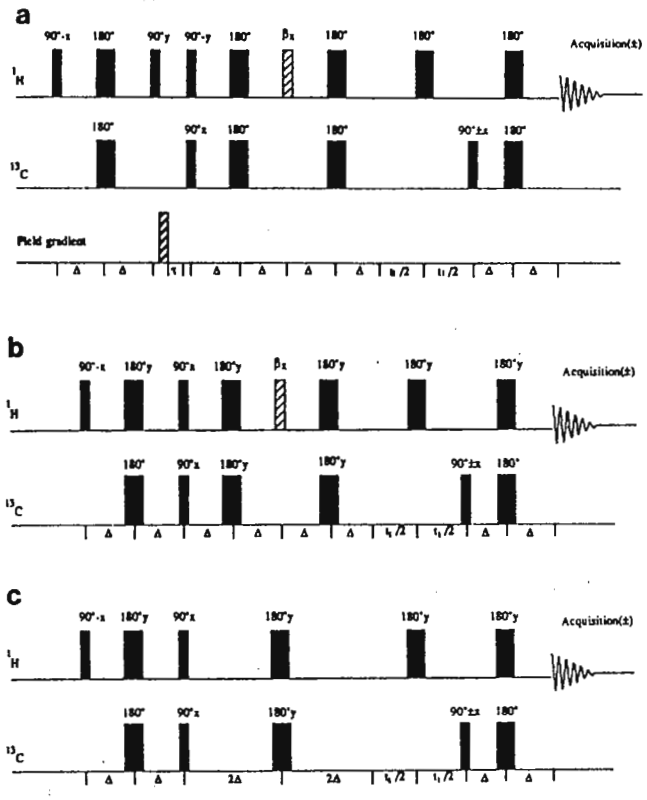
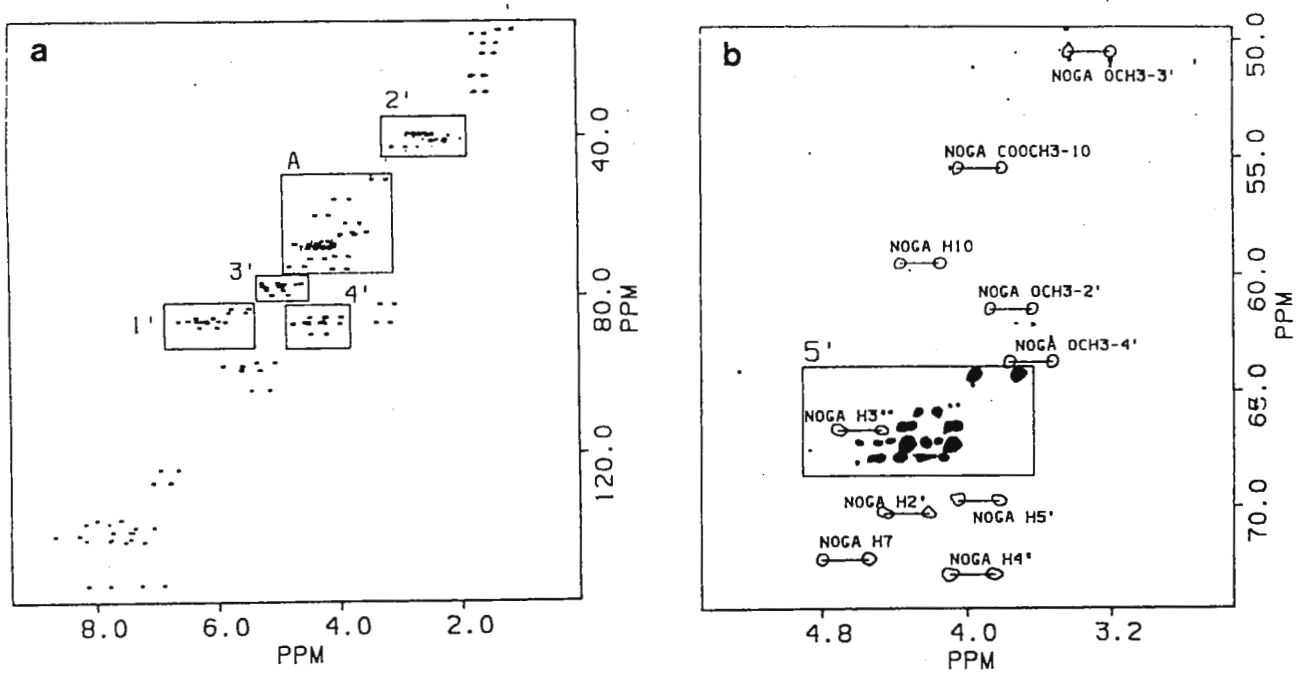


Figure 1. The pulse schemes of the editable heteronuclear multiple-quantum correlation (E-HMQC) experiments. a) using field gradient to suppress undesired ^{12}C-bonded 1H signal. b) flipping undesired ^{12}C-bonded proton magnetization back to the z axis. c) simplified form of Scheme b.

Figure 2. a) The ^{1}H-^{13}C E-HMQC spectrum of 4 mM natural abundance Nogalamycin2-d(AGCATGCT)2 complex in 0.45 ml D2O buffer solution, which contains 0.1 M NaCl, 10 mM phosphate, and 0.1 mM EDTA. The experiment was performed with Scheme c in Figure 1 without ^{13}C decoupling. The spectrum was recorded at 30.0 °C on the Bruker AM600 spectrometer. The 2D FIDs were recorded with 512x2048 real points, acquisition times of 21.3 ms in t1 and 170 ms in t2, 160 scans per t1 increment, and a total acquisition time of 25 hours. The delay of Δ was set equivalent to JCH=145 Hz. b) The expansion of Box A in a). In this spectral region, the cross peaks from CH and CH3 groups of nogalamycin are positive and are shown in open contours as indicated, while the cross peaks from the 5' CH2 groups of DNA are negative and are shown in filled contours.



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§ Present address: Pharmaceuticals Division, CIBA-GEIGY Corporation,
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Dr. Bernard L. Shapiro
TAMU NMR Newsletter
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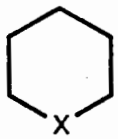
MERCK
Research Laboratories

Deceptions of Nature: Hazards in Low Level nmr Analysis

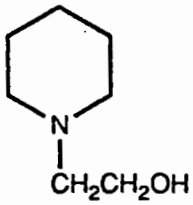
(received 2/17/94)

Dear Barry,

Recently we were involved in evaluating fractions from a fermentation which produced an agent showing coccidiostatic activity. Several bioactive fractions were characterized by five aliphatic multiplets with relative areas from low to high field of 1,1,2,2,1. To facilitate further studies the five fractions, each containing about 10 μg, were combined and the resulting spectrum is shown in figure 1. Irradiating the 3.80 ppm triplet collapsed the 3.12 ppm triplet to a singlet indicating that both were methylenes which established that the proton complement was 2,2,4,4,2. The pattern 4,4,2 is generally diagnostic of a six membered ring heterocycle with the appearance of the spectrum determined by the heteroatom.



The chemical shift of 3.00 for the two α methylenes suggested that X might be a plus-charged nitrogen and the correspondence with the spectrum of piperidine hydrochloride (figure 2) was reassuringly close. Based on the chemical shifts of the dimethylene protons and the fact that this group had to be attached to the nitrogen, the N-β-hydroxyethylpiperidine structure was proposed.



Further support for a positively charged nitrogen was provided by the upfield shifts of the 3.00 ppm and 3.12 ppm signals upon addition of alkali.

A search of the patent literature disclosed that the proposed structure was patented by Merck as a coccidiostat! This was good news and bad news. The good news was that the reputation of the spectroscopist went sky-high among the biochemists for arriving at a structure solely from nmr which turned out to have the biological activity known to be present. The bad news was that one could not expect credit for reinventing the wheel.

Dr. Bernard L. Shapiro
Page 2

It remained only to confirm the proposed structure by a direct comparison with an authentic specimen. The spectrum of a commercial sample of free base (figure 3) showed the expected similar profile, the differences reasonably attributed to the absence of a positive charge on the nitrogen. Identity of the two products would be established if the spectrum of the combined solutions showed that all characteristic peaks superimposed. Given the foregoing findings there was little reason to doubt the outcome. Hence, it was a shock when the spectrum (figure 4) revealed that the two substances were different. A bigger shock followed two weeks later when an overnight experiment on a metabolite showed, in addition to signals from the metabolite, a series of five multiplets suspiciously similar to those in figure 1. A blank run on our D_2O indicated that our proposed structure was merely an extremely low-level contaminant in our solvent.

This sequence of events gives new meaning to the term "red herring". The chance of an artifact mimicking the spectral features of any therapeutic agent is most unlikely. The odds against its mimicking a structure having the biological properties known to be present would seem to be astronomical.

This is yet one more example of the rule that purity requirements vary inversely with sample size. We now have initiated a policy of segregation in which solvents and nmr tubes are set aside to be used exclusively for very low-level samples. Separate tubes minimizes the risk of accidental contamination from incomplete cleaning of tubes used for milligram sized samples. Prior to use an overnight spectrum is obtained on all new lots of "100%" solvents so that the above described embarrassment will never recur.

Byron

B. Arison - 594-5394

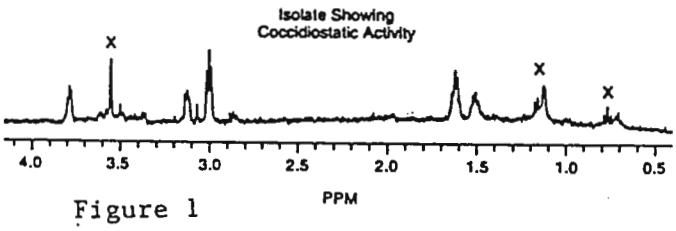


Figure 1

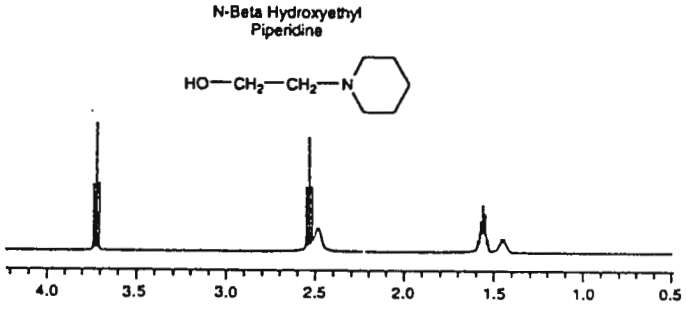


Figure 3

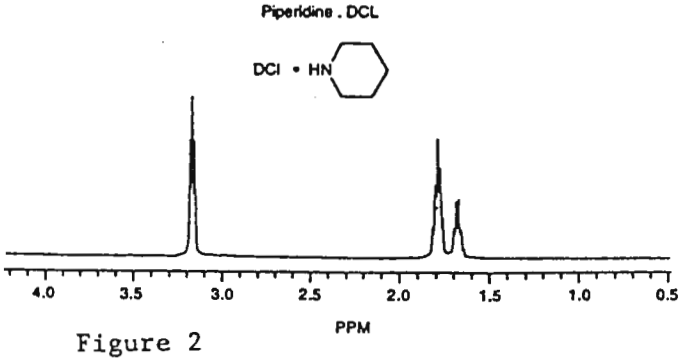


Figure 2

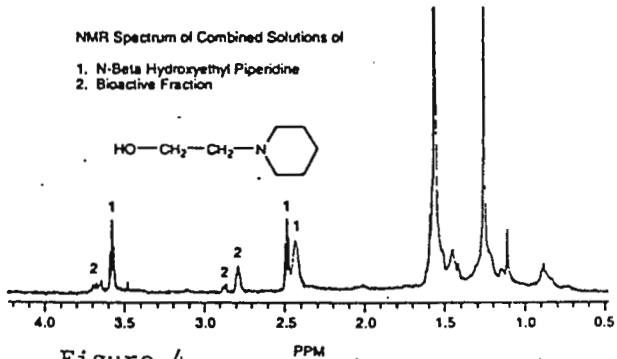


Figure 4

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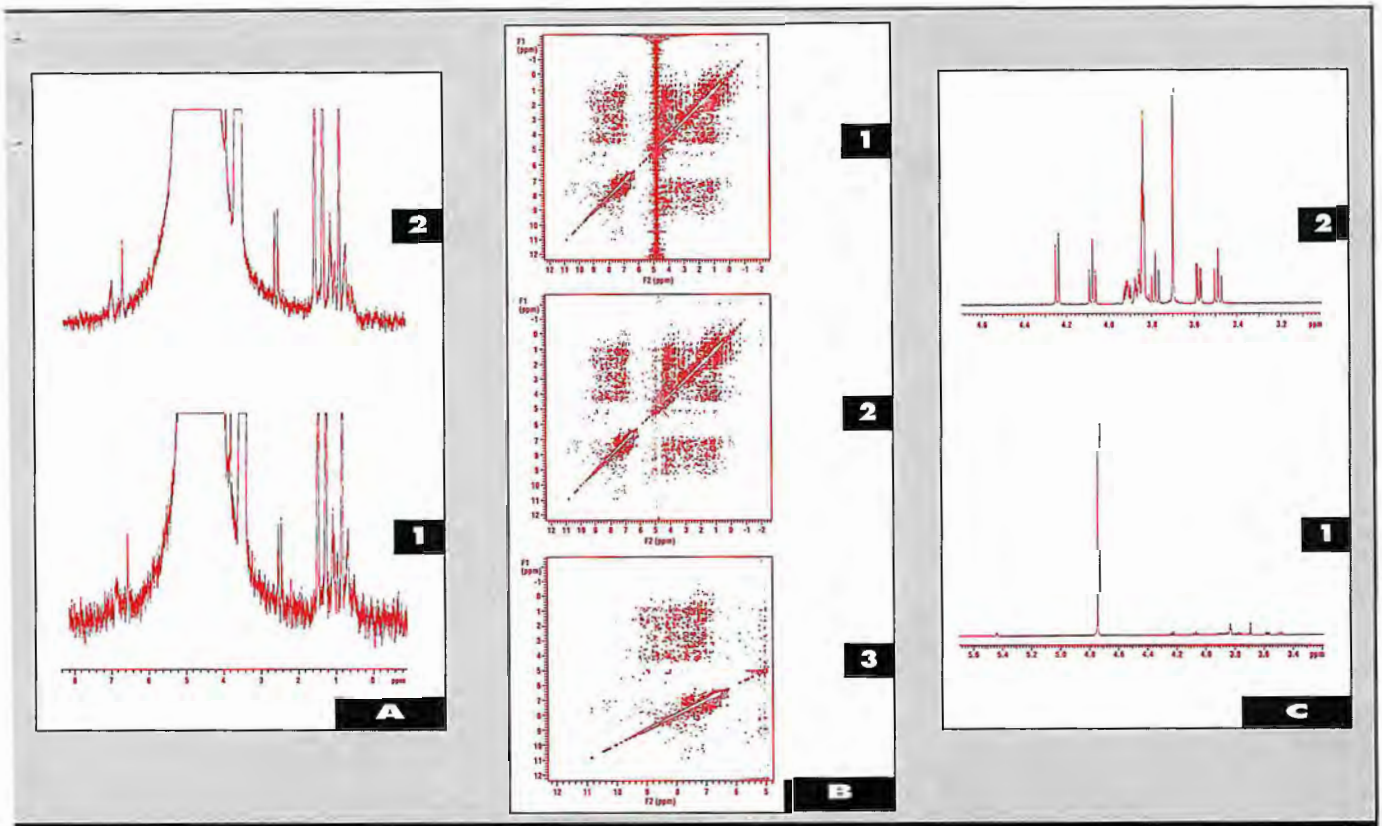

*All spectra above were obtained with UNITY*plus *NMR spectrometers: A1) Spectrum of dilute commercial soap solution in H_2O, collected using a 5 kHz analog filter. A2) Spectrum of dilute commercial soap solution in H_2O collected using oversampling and digital filtering. B1) Water-suppressed NOESY spectrum of 1 mM lysozyme in 90% H_2O. B2) Water-suppressed NOESY spectrum of 1 mM lysozyme in 90% H_2O using digital filtering solvent subtraction to remove the residual water signal. B3) Water-suppressed NOESY spectrum of 1 mM lysozyme in 90% H_2O using digital filtering to restrict data acquisition to the fingerprint region. C1) 300 µg of sucrose in D_2O, spectral width 10 kHz. C2) 300 µg of sucrose in D_2O, using digital filtering to restrict the spectral width to 1 kHz, with elimination of the HDO signal.*

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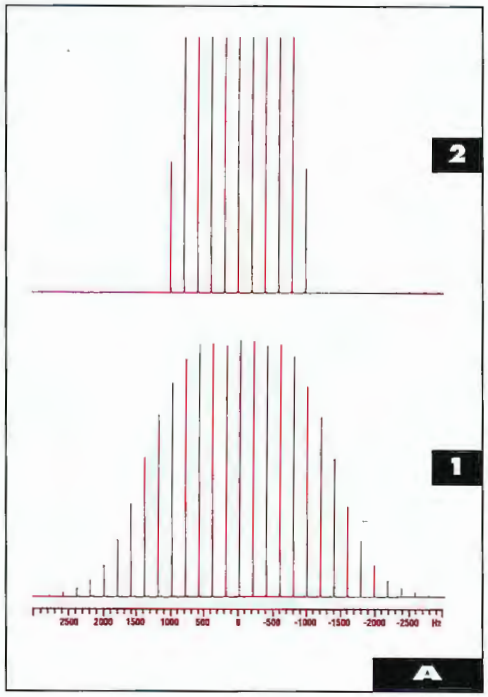
Figure A: Varian's digital filters provide both very sharp signal cutoff response at the edges of the bandwidth and extremely flat signal response within the chosen bandwidth.
A1) Profile of the signal amplitude response for a 1 kHz analog filter
A2) Profile of the signal amplitude response for a 1 kHz digital filter.



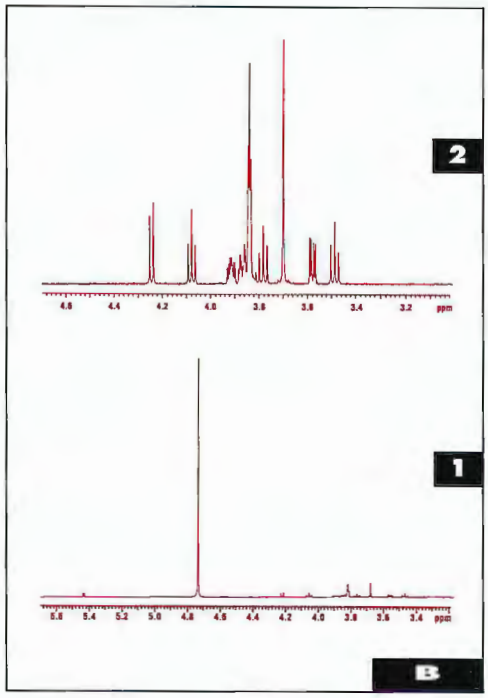
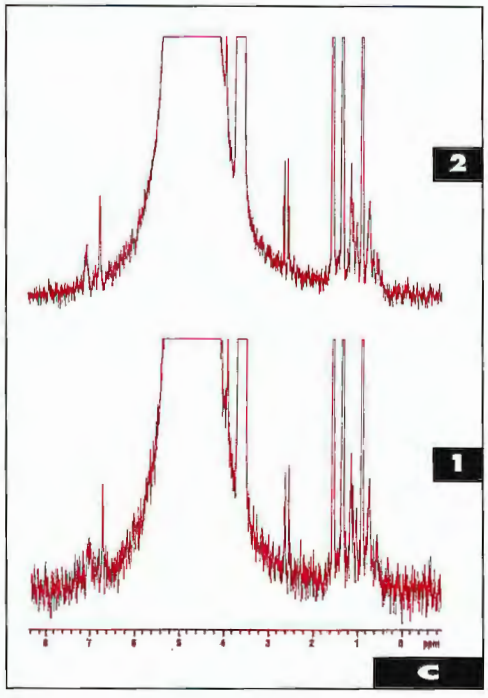


Figure B: Varian's digital filters provide the capability to limit the spectral width to a region of interest without introducing aliasing artifacts.
B1) 300 µg of sucrose in D_2O, spectral width 10 kHz
B2) 300 µg of sucrose in D_2O, using digital filtering to restrict the spectral width to 1 kHz, with elimination of the HDO peak.

Figure C: Varian's digital filters provide increased sensitivity for low level signals in high dynamic range samples.
C1) Spectrum of dilute commercial soap solution in H_2O, collected using a 5 kHz analog filter.
C2) Spectrum of dilute commercial soap solution in H_2O collected using over-sampling and digital filtering.



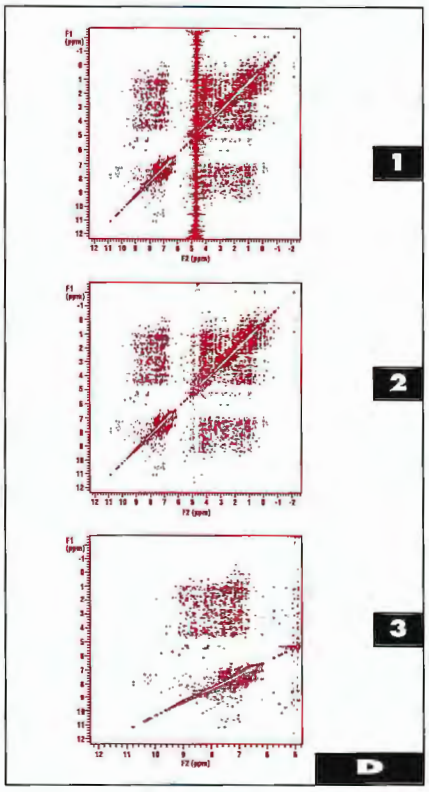


Figure D: Varian's digital filters can be applied during data processing or data acquisition.
D1) Water-suppressed NOESY spectrum of 1 mM lysozyme in 90% H_2O.
D2) Water-suppressed NOESY spectrum of 1 mM lysozyme in 90% H_2O using digital filtering solvent subtraction to remove the residual water signal.
D3) Water-suppressed NOESY spectrum of 1 mM lysozyme in 90% H_2O using digital filtering to restrict data acquisition to the fingerprint region.

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The Case of the Invisible Methylene

January 28, 1994 (recd. 2/3/94)

Dear Barry:

One of the greatest worries of the day to day practicing NMR spectroscopist is providing incorrect structural information based on results derived from routine spectra. We recently encountered an example where this could have happened to us, but for fortune. In the case described here, a combination of routine ^{1}H, ^{13}C and DEPT spectra suggested that a particular carbon in a compound of interest was quarternary. Fortunately, however, this assignment was inconsistent with other information available. As it turns out, the "quaternary" was a methylene carbon. We would like to share this experience with your readers.

Shown below in Fig.1 is the relevant structural fragment. At 400 MHz and 25° in $CDCl_3$, the two protons at C-2 appear as a broad multiplet (2.7 ppm) while no obvious (except in hindsight) resonance is observed that would correspond to protons on C-1 (Fig.2e). In the ^{13}C spectrum (Fig. 3d), C-1 (24 ppm) and C-2 (30.6 ppm) are sharp and the DEPT spectrum (Fig. 3c, $\theta = 135°$) clearly indicates that C-2 is a methylene. C-1, however, appears to be a quaternary. As stated above, this assignment was inconsistent with other data, so we decided to look at the spectra as a function of temperature.

As the sample was cooled progressively from 25° to -25°, the proton NMR spectrum was observed to change dramatically (Fig. 2). At the lowest temperature, relatively sharp multiplets appeared (3.3, highly overlapped, and 2.3 ppm) which were assigned to the C-1 protons. In addition, the broad resonance for C-2 broke into two resonances (2.6 and 2.9 ppm, the latter overlapped with other peaks). When the DEPT spectrum was repeated at -30° (Fig.3b) the carbon peak at 24 ppm revealed its true identity to be a methylene. Apparently, at 25° the short, exchange induced T_2 causes the magnetization due to C-1 protons to decay to zero by the end of the 1/J DEPT delay (7 ms), thereby giving rise to no signal. Note also that the 25° undecoupled ^{13}C spectrum (Fig. 3a) correctly identified the 24 ppm peak as a methylene without the need for more "modern" techniques.

We are currently working to identify the exchange process responsible for this effect.

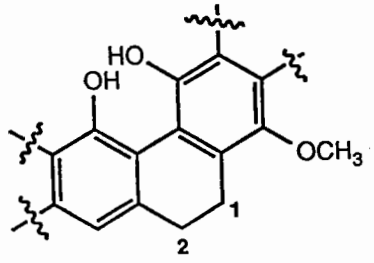


Figure 1

Sincerely,

Min Chu

Tze Ming Chan

Mohindar S. Puar

C. Anderson Evans

Figure 2

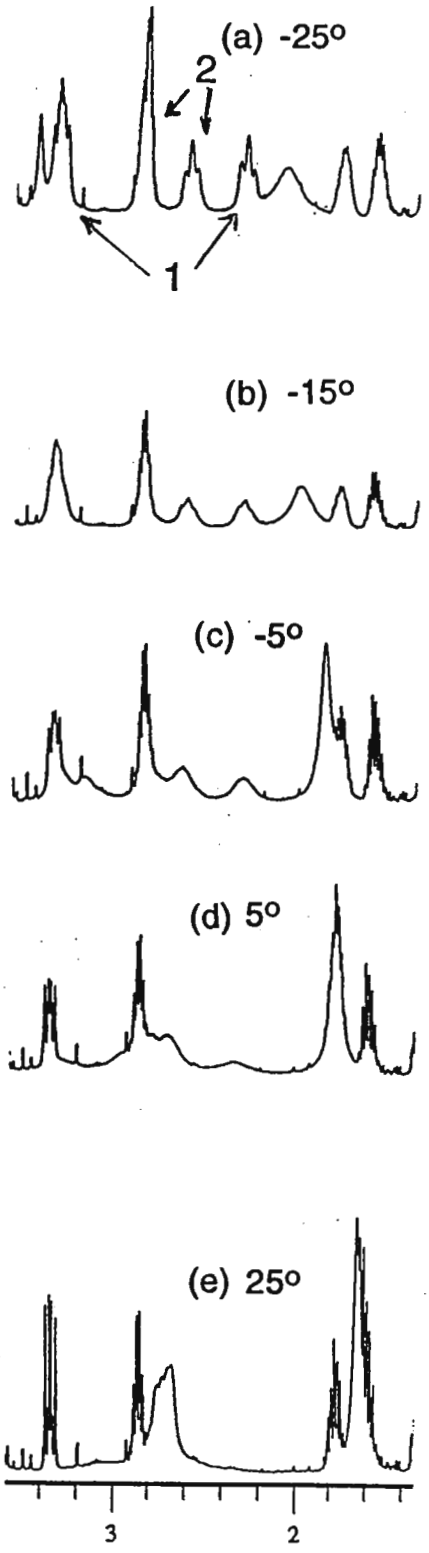
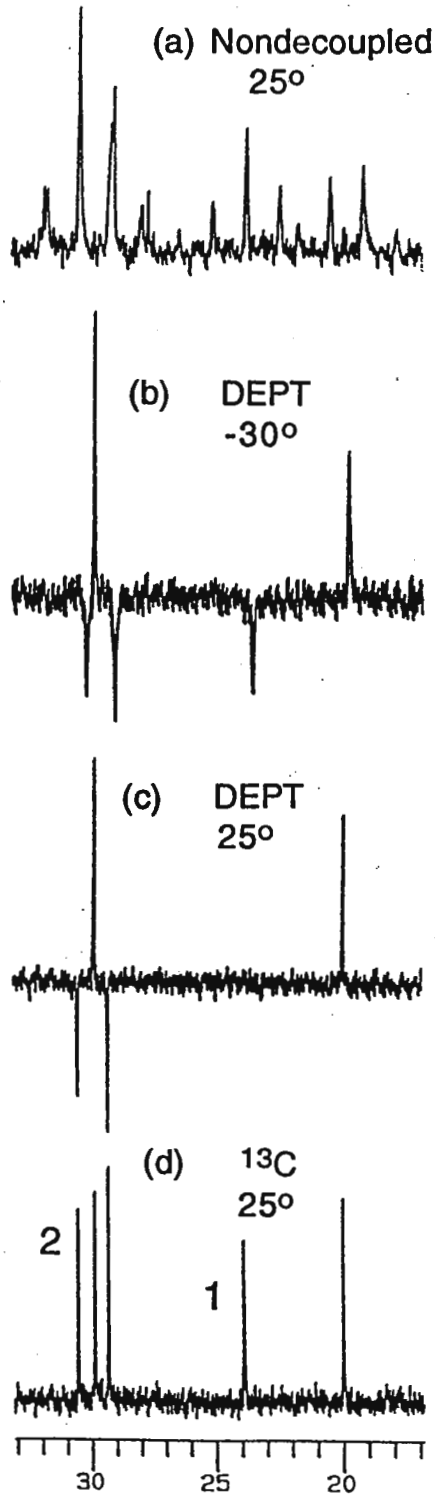


Figure 3



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FRANCE

La Tronche, January 20, 1994
(received 1/26/94)

ABOUT THE USE OF HIGH RESOLUTION ^{14}N-NMR FOR THE IDENTIFICATION OF LIPID SPECIES IN CEREBRAL EXTRACTS.

Dear Pr Shapiro,

One of the problems arising when the study of lipid extracts of cerebellum are undertaken is the identification of the main classes of lipids, gluco- and phospholipids. ^{1}H-NMR spectroscopy was the firstly used, due to its intrinsic sensitivity. Unfortunally the main part of the spectra is strongly overlapped by the resonances of cholesterol, and several informations , i.e. the chain length and unsaturation could only be drawn from these experiments (1). ^{13}C-NMR experiments gave further informations about the acyl chains and the glycerol moieties (2) and allowed the identification of several species (phosphatidyl choline and -ethanolamine for instance). Furthermore several resonances of the glucidic part of the glucolipids in the 45-76 ppm and 80-110ppm regions could be identified after a careful analysis. Despite the severe overlapping of the methine and the carbonyl groups resonances, those attributed to the chains of the glucolipids could also be partially attributed . Thus we tried to estimate the relative importance of gluco- and phospholipid composition by using ^{14}N-NMR. Since ^{14}N has a spin different from 1/2 (I=1), the lineshape and relaxation is generally governed by electron field gradient in organized systems. Under theses conditions no information is easily obtained in terms of chemical shift. However the very few studies published on the subject (3-4) showed that high resolution spectra can be obtained when fast isotropic motions occurs, such as in liquids .

We present here a ^{14}N-NMR spectrum (bottom) of a total lipid extract of a cerebellum recorded at 28MHz (9.4T). The attribution of the two groups of resonances was obtained by recording similar spectra of pure phospholipids (the ^{14}N resonances of ethanolamine, choline and serin are very close and constitute the upfield group of resonances) , or ceramide as a model of sphingolipid (the amide resonance is found at the downfield part of the spectrum). These two resonances are present on the spectrum recorded on sphingomyelin, a sphingolipid bearing a phosphocholin headgroup. We hope, if any quantitation of such spectra is possible, to obtain an appraoch of lipids metabolism perturbations associated with pathological situations -i.e. tumour or ischemia-.

Sincerely yours,

J.C.DEBOUZY, F.FAUVELLE, C.NEMOZ E.SAM-LAI

(1) I.L. Kwee, T.Nakada and W.G.Ellis, Magn.Res. in Medicine(1991), 21:49-54.
(2) U.Sonnewald, N.Westergaard, E.Isern, T.B.Müller, A. Schouboe, S.B.Petersen and G.Unsgard, Int.J. of Oncology, (1993), 2: 545-555.
(3) T.A.Thorpe, K.Bagh, A.J.Cutler, D.I.Dunstan, D.D.Mc Intyre, and H.J.Vogel, Plant.Physiol. (1989), 91:192-202.
(4) U.P.Lungberg, R.G.Weich, P.Jensen, H.J.Vogel, Plant.Physiol. (1989), 89:1380-1387.

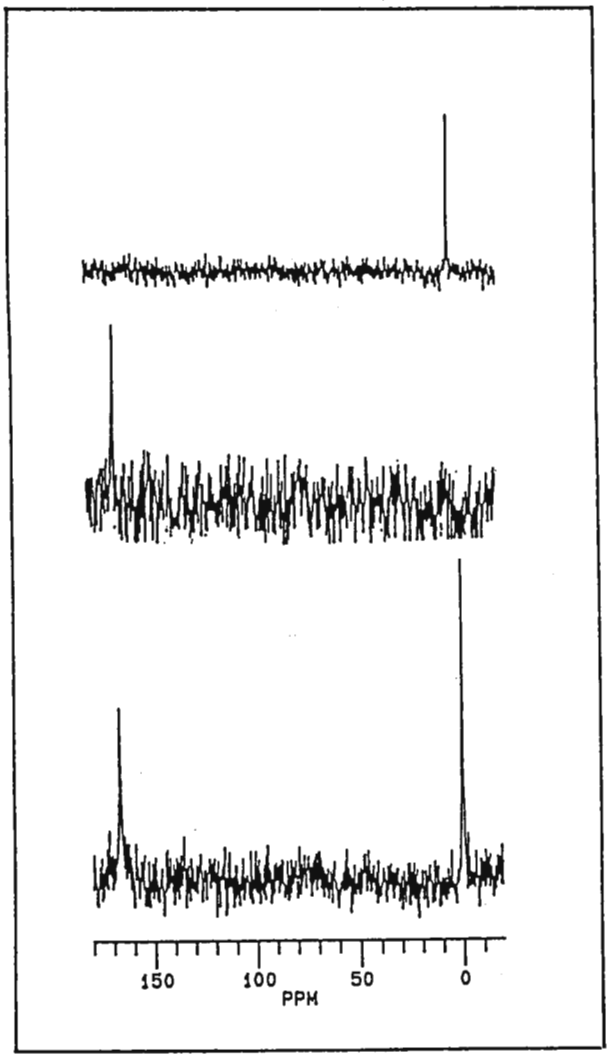

Figure 1/ ^{14}N-NMR spectra of bottom) total lipid extract of cerebral tissue in $CDCl_3$, middle) of pure ceramide , top) of phosphatidylcholine/phosphatidylethanolamine mixture.

Postdoctoral Position Available: Solid State NMR Spectroscopy

There is an opening in my lab for a person to work on applications of solid state nmr to the study of materials. Requirements are a Ph.D. in Chemistry or Physics and some familiarity with solid state CPMAS NMR methods. Familiarity with Varian Sun-based (VXR/UNITY) instruments is also advantageous. A one year appointment is available immediately, with renewal for a second year based upon availability of funds and mutual agreement. Three instruments are available for this work; a home-built 200 MHz solids instrument, a Unityplus-200 instrument dedicated to solids, and a Unityplus-600 with a supersonic MAS solids accessory. Between these instruments we have the capability to perform triple resonance solids experiments such as REDOR, variable temperature (-150° to + 250°), multinuclear experiments, and wide-line NMR. Interested applicants should have at least two letters of reference, cv, and copies of publications sent to: Prof. Peter Rinaldi, Department of Chemistry, The University of Akron, Akron, Ohio 44325–3601. (cv's can be sent to plr@atlas.chemistry.uakron.edu).

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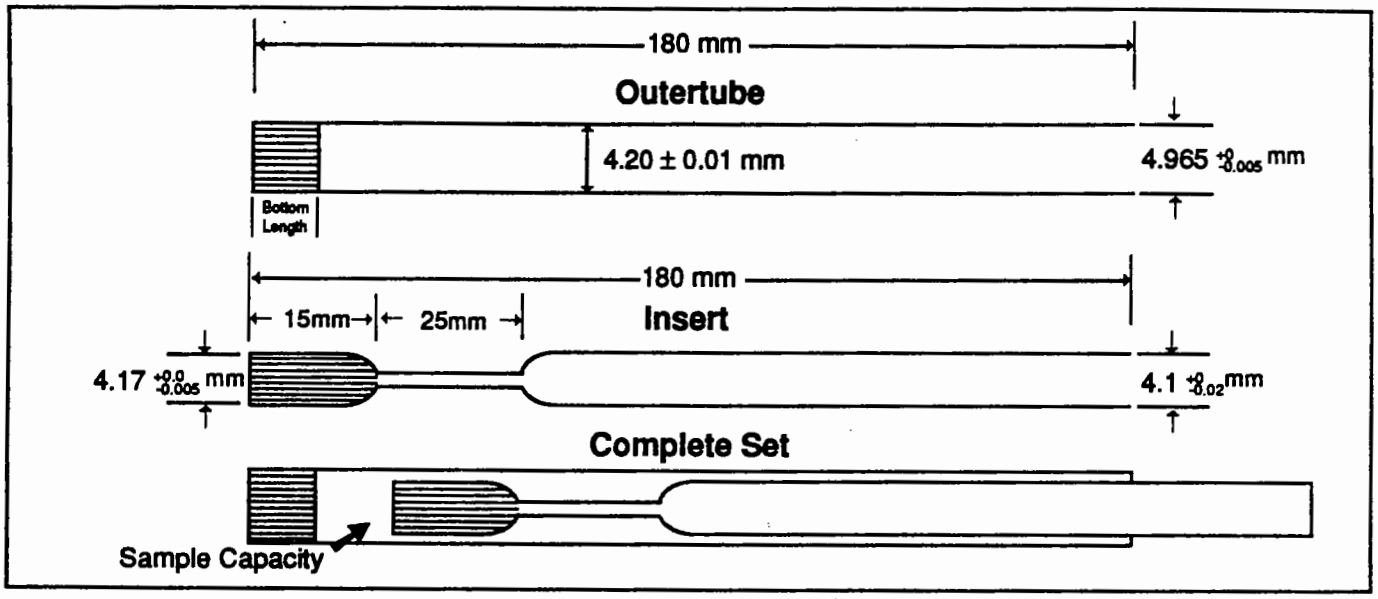

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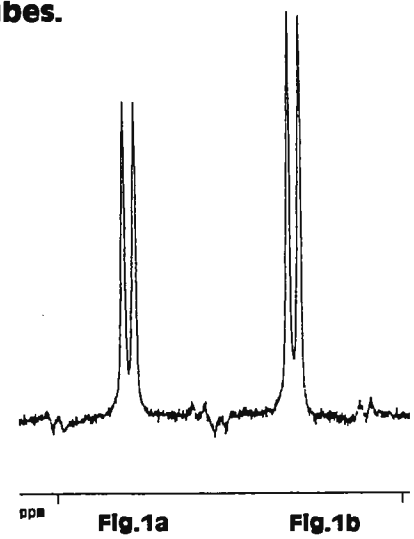
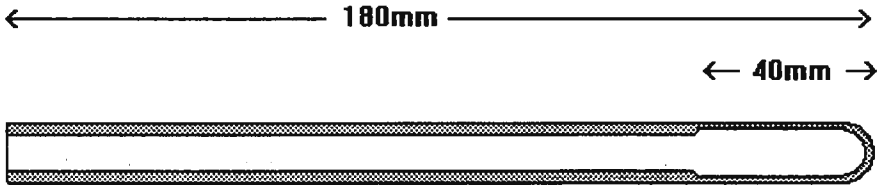


Fig.1a Fig.1b

The spectra of 20mm sucrose in D_2O were obtained with a single scan without apodization prior to Fourier transformation on a Bruker AMX-600 spectrometer at 298 K. By using Shigemi high quality 5mm standard tube (Fig.1a) and the Shigemi highly sensitive thin wall 5mm tube (Fig.1b), the spectra confirms a sensitivity enhancement of about 10%.



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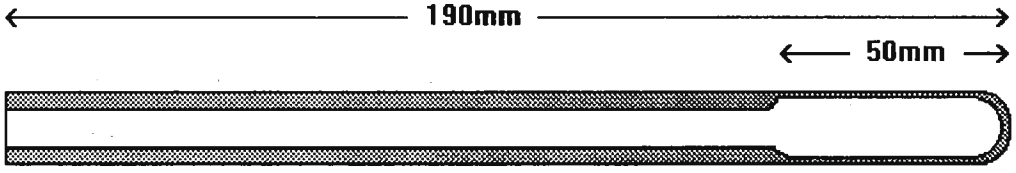

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February 4, 1994 (received 2/14/94)

CNRC · NRC

Dr. B.L. Shapiro
TAMU Newsletters
966 Elsinore Court
Palo Alto, CA 94303
USA

Generalized Curve Fitting for the Analysis of Relaxation Data

Dear Dr. Shapiro,

NMR relaxation parameters contain a wealth of information about dynamic properties of molecules under study. We are using the spin-spin relaxation rates for the estimation of k_{off} *in systems*

$$L+P \rightleftharpoons LP$$

where L is a small ligand (peptide), P is a large substrate (protein) and LP is a complex between them. It is often hard to find a singlet in ^{1}*H-spectra of peptides or proteins that would be suitable for* T_2 *experiments. There may be number of doublets but it is not possible to use the CPMG spin-echo method because of the cosine modulation of the resonance intensity decay. We utilize Norwood's approach to substitute the multiple echo method by the z-filtered one-echo pulse sequence (Norwood T.J., JMR Series A, 101, 109 (1993)). Experimental data are processed using the following equation for curve fitting*

$$I(t)=I(t_0)\cos(\pi J_{kl}t)e^{-t/T2}$$

Bruker company delivers a software package for the calculation of T_1 *and* T_2 *relaxation times but with no allowance to incorporate cosine modulations. The software package FELIX does not offer the option for the calculation of relaxation times. We decided to create our own programs for this purpose.*

Experimental data from our AMX 500 NMR spectrometer are processed in FELIX (Hare Research Inc., Seattle, WA) by a series of macros following the concept of saving 1D spectra into a matrix for more convenient handling. The next step includes the creation of an ASCII file that contains intensities of particular resonances. This ASCII file serves as an input for a home-made program utilizing the Levenberg-Marquardt least-square algorithm for nonlinear fitting (Press W.H., Flannery B.P., Teukolsky S.A., Vetterling W.T.: Numerical Recipes in C., Cambridge University Press, Cambridge 1988). The advantage of this approach is the larger flexibility in comparison with the Bruker software.

One example of the curve fitting of T_2 *experimental points for an 11 residue peptide (*$Ile_{\gamma(CH3)}$*) is given in Fig. 1. The coupling constant is 6.8 Hz and the spin-spin relaxation time is 181 ms. Fig. 2 contains the curve fitting for selective* T_1 *experimental data of the same peptide (*Tyr_{NH}*). The spin-lattice relaxation time is 333 ms.*

Sincerely Yours,

Richard Hrabal
NMR Laboratory

Hervé Hogues

Feng Ni

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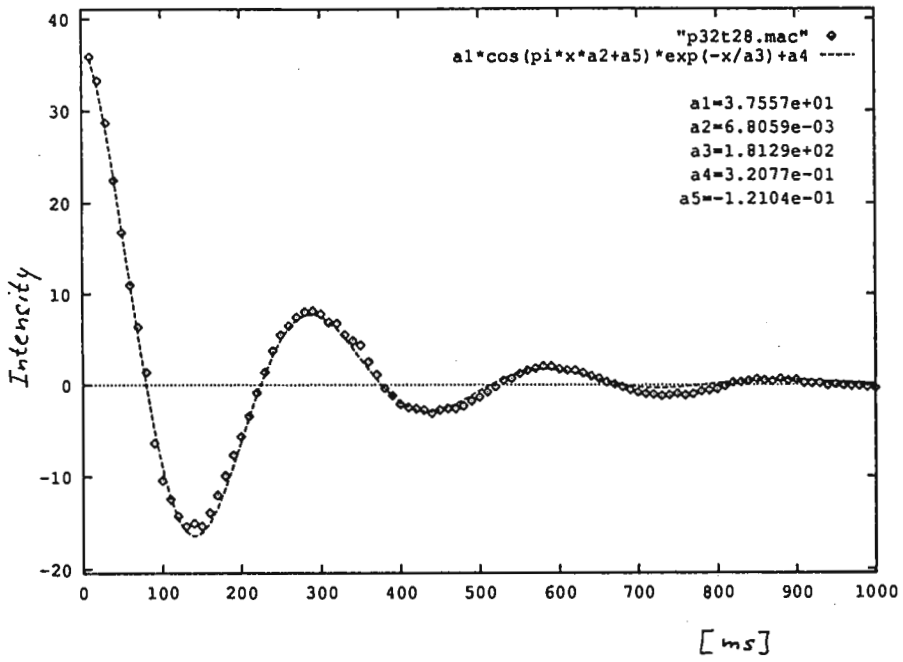
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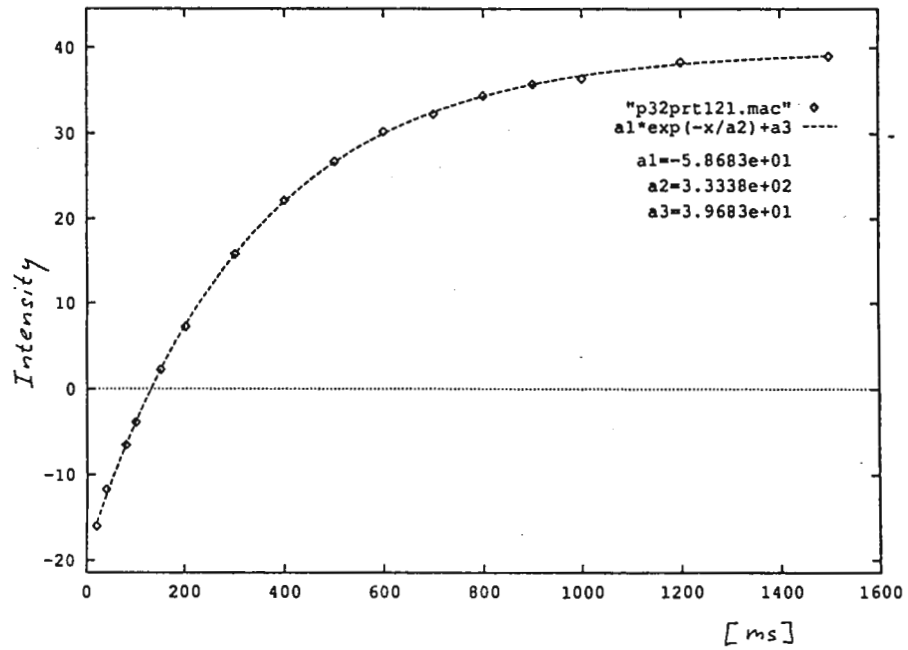
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[ms]

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INSTITUT DE CHIMIE MINÉRALE ET ANALYTIQUE
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Prof. Bernard L.Shapiro
966 Elsinore Court
Palo Alto, CA 94303
U S A

31 January, 1994
(received 2/4/94)

FIRST HIGH-PRESSURE, HIGH-RESOLUTION PROBE FOR NORMAL BORE SUPERCONDUCTING MAGNETS

Dear Prof. Shapiro,

For many years we have been developping high-pressure, high-resolution NMR probes using pressure vessels. in our institute A first probe design for wide-bore 4.7 T magnets was published in 1983.[1] In 1990 we built the first probe of this kind for a 9.4 T wide-bore magnet working up to 400 MHz.[2] About two years ago we had to replace the old 4.7 T wide-bore magnet by a normal-bore one. We decided therefore to construct a high-pressure probe for this type of magnet. Further advantages of the smaller diameter are the possibility to extend the frequency range by using higher field magnets (14.1 T), the easier shimming and the reduced weight, making this probe much convenient.

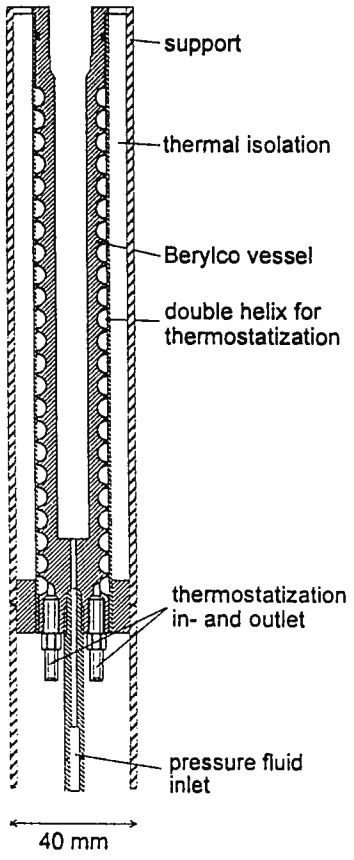

Fig. 1 Schematic drawing of the normal-bore multinuclear high-pressure probe

The Figure 1 shows the first high-pressure high-resolution probe fitting into a normal-bore (40 ∅ mm) cryomagnet. At the moment it works up to frequencies of 200 MHz and features the possibility of a ^{2}H lock. The pressure vessel is machined from Berylco-25 and has an external diameter supporting the pressure of 16 mm, an inner diameter of 11 mm at the level of the coil and an inner length of 140 mm. A double helix is cut at the outside the vessel for circulation of the thermostating liquid.

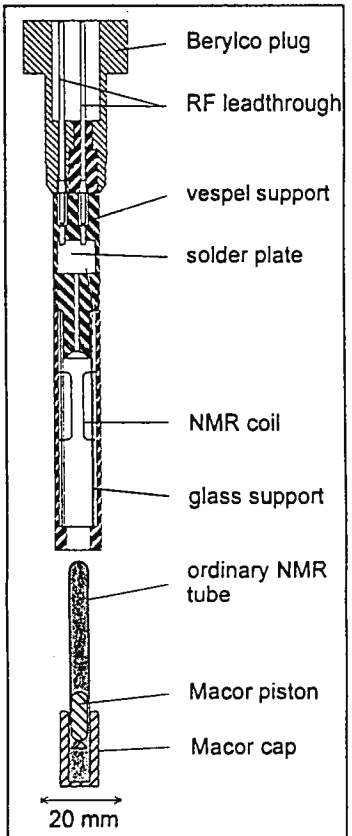

Fig. 2 Schematic drawing of the NMR insert and the sample container

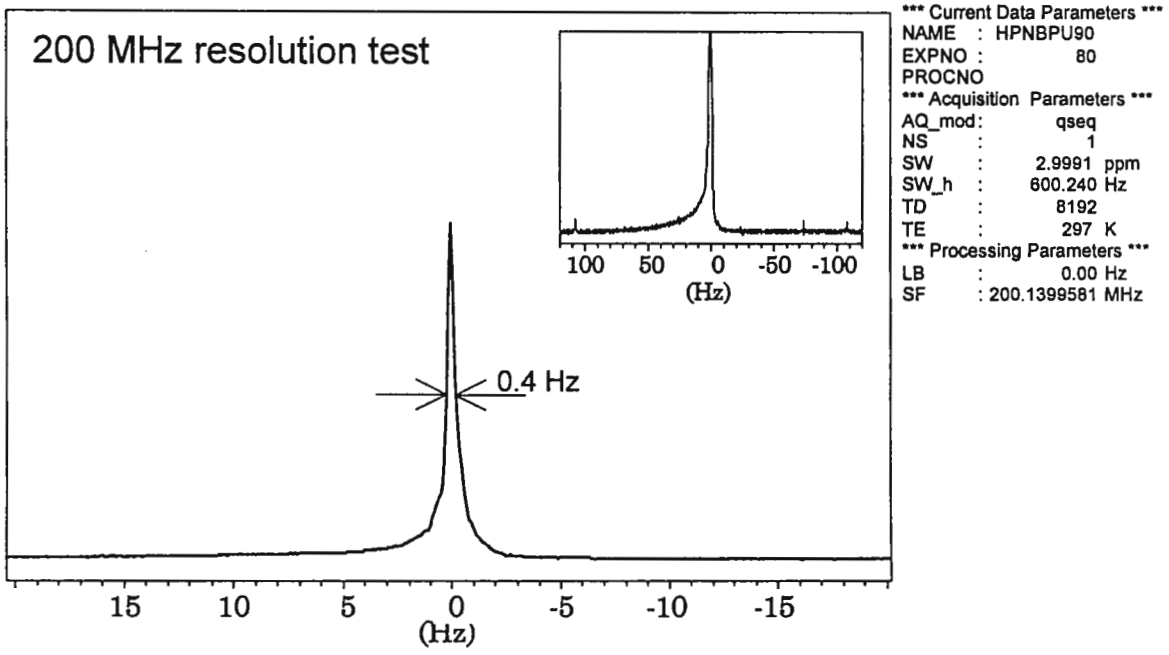

Fig. 3 Resolution and lineshape test performed at 200 MHz ^{1}H resonance using $CHCl_3$ in acetone-d6 (room temperature, ambient pressure)

Two NMR inserts with NMR coils having 2 or 4 turns were built to obtain maximum sensitivity at various observation frequencies. The sample container is an ordinary 5 mm Wilmad tube, cut to a length of 50 mm. Closing and pressure transmission is achieved by two mobile macor pieces, a piston and a cap. The sample volume is about 1ml. The resolution obtained is about 0.5 Hz (^{1}H, 200 MHz, no sample spinning).

B. Moullet L. Helm A.E. Merbach

[1] D.L. Pisaniello, L. Helm, P. Meier, A.E. Merbach, J.Am.Chem.Soc. 105, 4528 (1983)
[2] U. Frey, L. Helm, A.E. Merbach, High Pressure Research, 2, 237 (1990)

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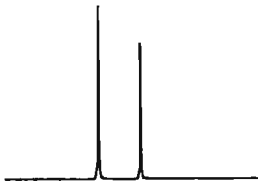
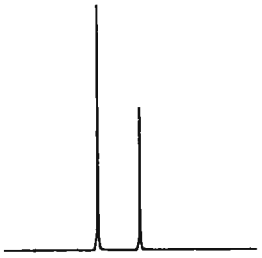
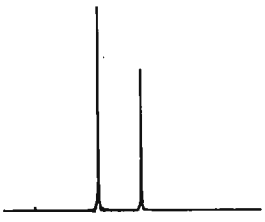


Variable amplitude cross polarization (VACP) *under* –2.6 KHz *mismatch condition*

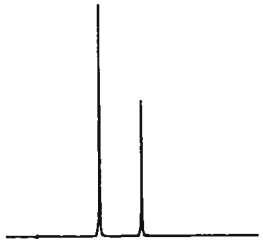
Deliberate "mismatch" of –1.9 KHz



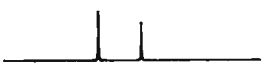
VACP *under normal match condition*



Normal "ideal" matched conditions



VACP *under* +2.0 KHz *mismatch condition*



Deliberate "mismatch" of +1.4 KHz

Chemagnetics would like to thank Professor Steve Smith for suggestion of this work and useful discussions during its implementation.

Francis Bitter
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Massachusetts Institute of Technology
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Telephone 617-253-

11 February, 1994
(received 2/17/94)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
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Palo Alto, Ca. 94303

Ferromagnetic Shimming of a 600 MHz NMR Magnet

Dear Barry,

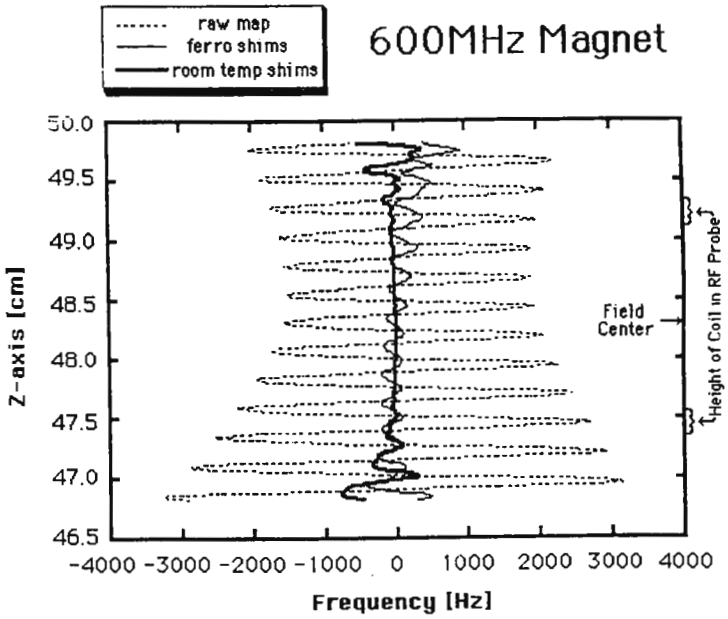
We thought we would drop you this note to fill your readers in on some interesting successes we have had with ferromagnetic shimming of a 14 Tesla NMR magnet built here in our lab. Unfortunately, this magnet initially had inadequate homogeneity for the high resolution studies for which we wished to use it. Most of the techniques we have applied evolved from research in the area of MRI magnets done here at MIT's Magnet Lab several years ago.

Three key technologies were used in shimming this magnet. First, the magnetic field inhomogeneities were mapped using a mapping system developed by Resonance Research Inc. to map the inhomogeneities with a high degree of accuracy. Second, a very powerful ferromagnetic shimming technique was developed and tested by researchers at the Francis Bitter National Magnet Lab. Third, a high performance room temperature shim system, built by Resonance Research Inc., was installed to shim out axial inhomogeneities through the 8th order and radial inhomogeneities to the 6th & 7th order.

The ferromagnetic shimming technique, as tested here at MIT has valuable implications for magnet suppliers throughout the world. Magnets which fail to meet the stringent requirements of high resolution NMR are currently dismantled or relegated to lower resolution types of research. Many more of these magnets might be made useful for high resolution experiments. While we do not recommend sacrificing good design and manufacturing practices, the availability of this additional shimming method will undoubtedly be of increasing importance as the cost of higher and higher field magnets rises.

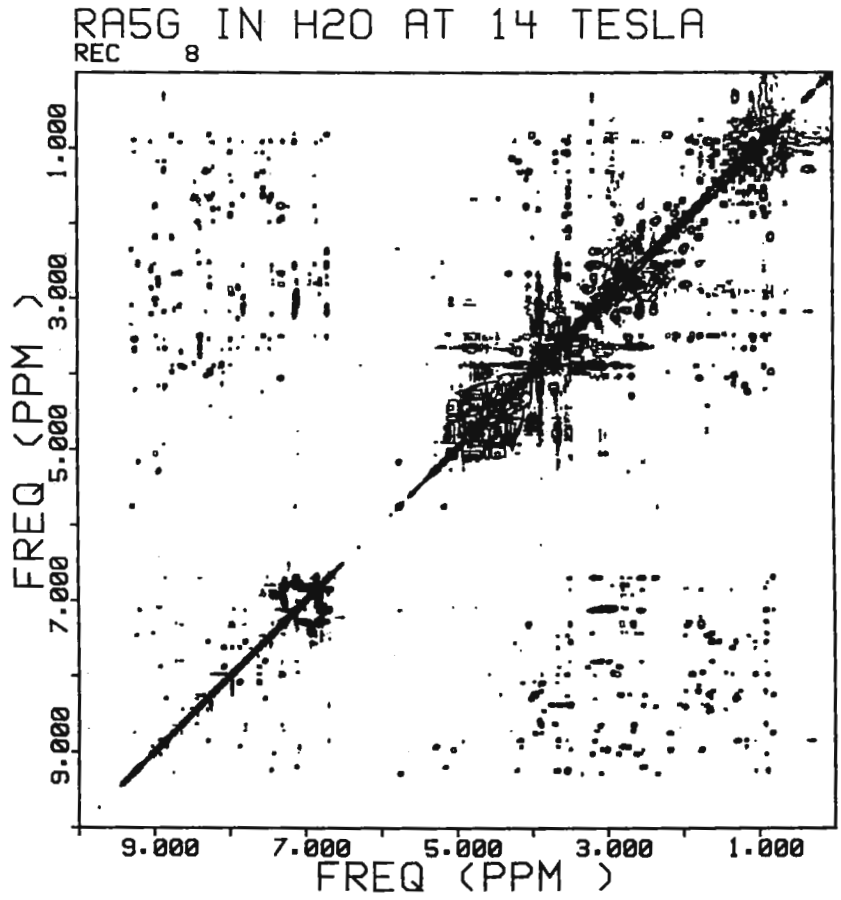
The computer code for designing the ferromagnetic shim matrix was developed by Bill Punchard for shimming whole body MRI magnets and modified by Emanuel Bobrov for designing a miniature set of shims for the MIT 600 MHz magnet. The results of this first attempt at ferromagnetic shimming were carried through the 3rd order, successfully reducing the largest inhomogeneities by more than 90%.

The map data on the right, reflecting a helical scan along the z-axis at a radius of 2.5mm, shows the dramatic improvements made by combining the ferromagnetic shim matrix and a room temperature shim system purchased from Resonance Research Inc. Over the central region of the map, the data reflects an improvement in field homogeneity of from 5 KHz to better than 20 Hz.



The field map shows that dramatic improvements were made, but by itself it cannot demonstrate the viability of the magnet for high resolution NMR work. Only through NMR experiments can this be shown.

To demonstrate the feasibility of acquiring proton spectra in water on a ferroshimmed magnet, we show a 2D NOESY spectrum of a ragweed allergen protein *Ambrosia trifida* measured in 90% H_2O / 10% D_2O.

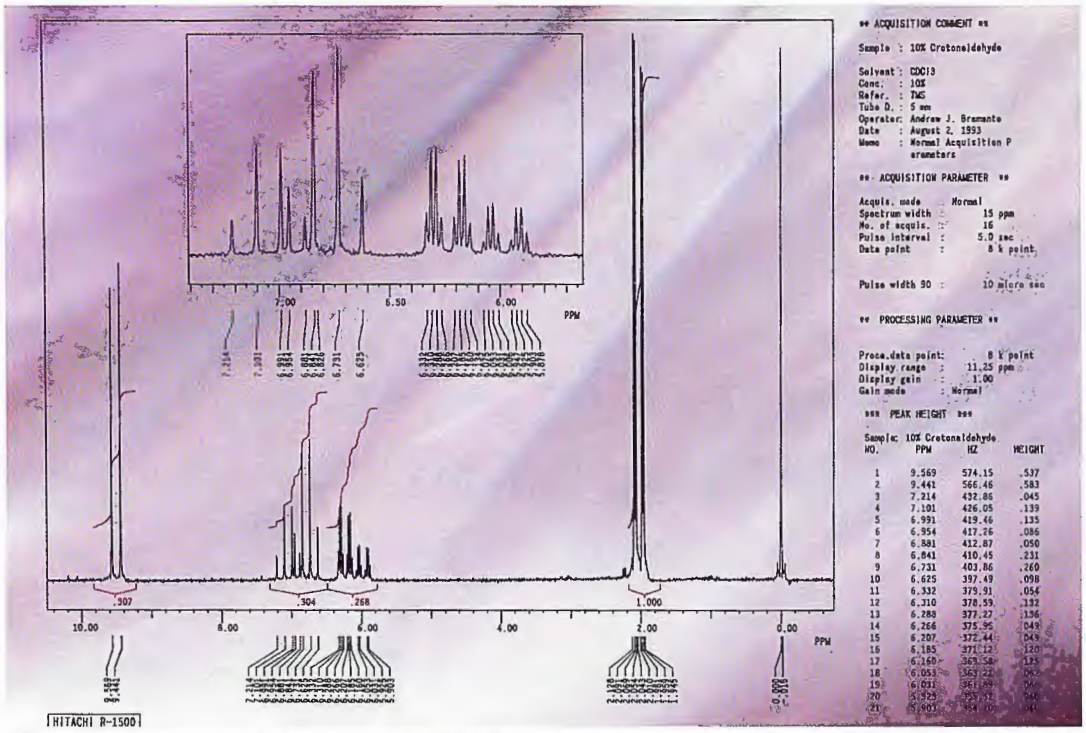


James J. Wrenn

Christopher J. Turner

William B. F. Punchard

Emanuel S. Bobrov



This R-1500 FT-NMR spectrum of crotonaldehyde represents a 16 pulse acquisition; each pulse was 10 μsec with a pulse interval of 5 seconds.

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February 10, 1994 (received 2/14/94)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinor Ct.
Palo Alto, Ca 94303

Title: 2D ^{29}Si NMR Investigation of the Structure of Dealuminated Mordenite.

Dear Barry,

We were interested in trying some of the 2D ^{29}Si NMR techniques which Colin Fyfe has popularized for the analysis of dealuminated zeolites in recent years. We had a sample of dealuminated mordenite (DAM) which seemed like a good candidate to test out our sequences. This sample had also been studied by Klinowski, [1.W. Kolodziejski, P.L.Barrie, H. He and J. Klinowski, J. Chem. Soc. Chem. Commun., 961 (1991)] using J-scaled COSY.

Mordenite is a zeolite that consists of 48 tetrahedral sites (t-sites) per unit cell (uc). There are four crystallographically distinct t-sites with the relative intensity ratio of 1:1:2:2. The data on DAM are summarized below.

t-site	#/uc	neighbors	TOT angle	Shift(calc)[a]	Shift(obs)
T1	16	T1, T1, T2, T3	150.4	-111.8	-113.0
T4	8	T2, T2, T3, T	152.3	-113.0	-114.0
T3	8	T1, T1, T3, T4	153.9	-114.0	-115.8
T2	16	T1, T2, T2, T4	158.1	-116.6	-116.0

a. δ = -0.6192 x (TOT angle) -18.68

The chemical shift calculated from the TOT angles would give the order of sites as T1, T4, T3, T2, but the differences in calculated values are small enough to make these assignments tentative. The peak at -113 ppm is due to either T1 or T2 because it is twice as intense as the -114 ppm peak, and it is assigned to the T1 peak because it has the smallest TOT angle. Since the T1 site has a T3 neighbor but no T4 neighbor, and the reverse is true for the T2 site, a COSY experiment should distinguish the correct order. Klinowski reported the order T1, T3, T2+T4, because his J-scaled COSY spectrum showed a cross-peak between the -113 and -114 ppm peaks.

Our double-quantum filtered COSY spectrum (Figure 1), although noisy, is better resolved in the region near the diagonal than was Klinowski's spectrum. We did not detect a cross-peak between the peaks at -113 and -114 ppm, which led us to assign the peak at -114 to T4 and the order of peaks to T1, T4, T2+T3. To confirm our T3/T4 assignment, the INADEQUATE spectrum shown in Figure 2 was obtained. Again we see no indication of coupling between the -113 and -114 ppm peaks. Although partially resolved, the peak at -116 ppm cannot be used with confidence to determine the relative shifts of the T2 and T3 sites.

Best Regards,

Joe Ray

G. Joseph Ray

Chris Cullen

Christopher H. Cullen

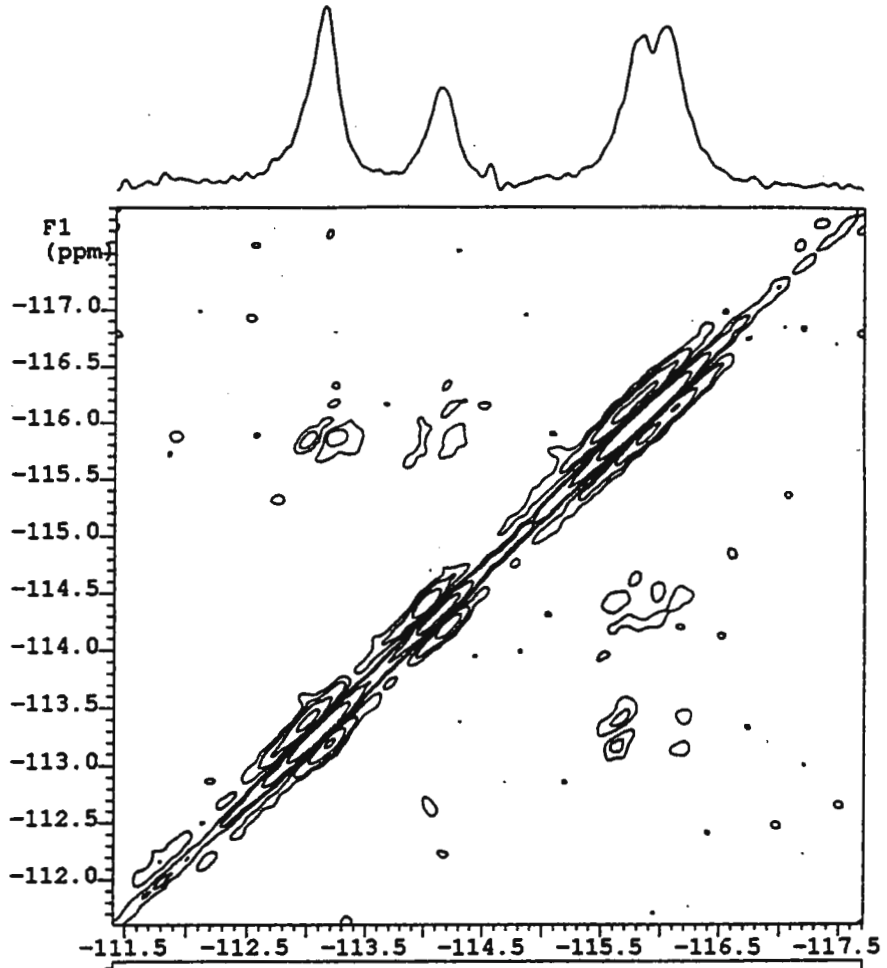

Figure 1.
^{29}Si Double-quantum filtered COSY spectrum.

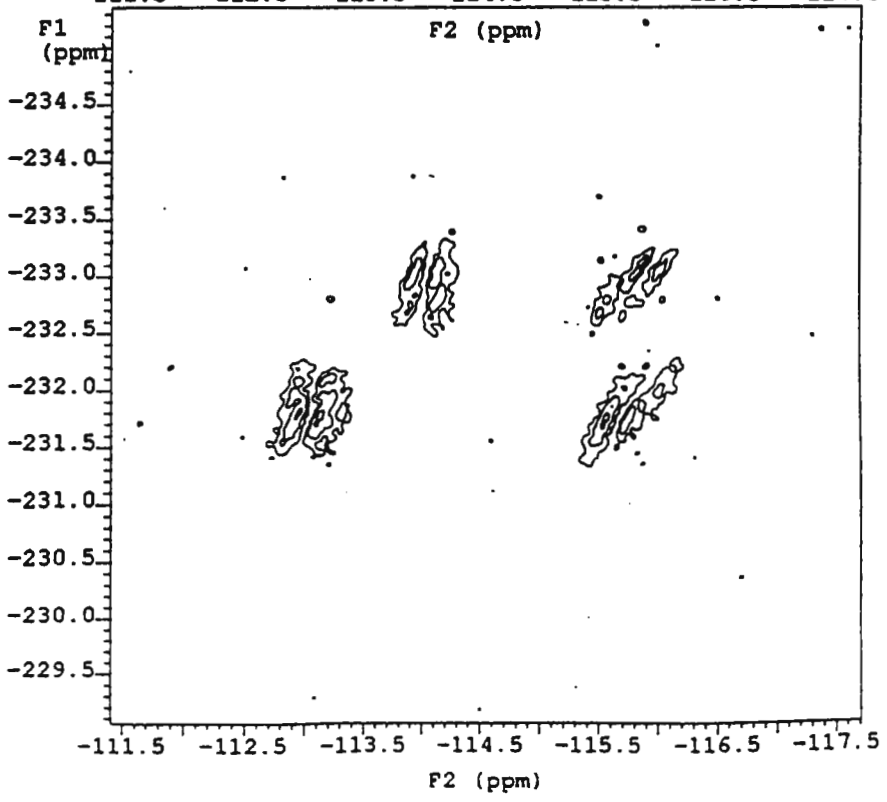

Figure 2.
^{29}Si INADEQUATE spectrum.

INRA
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63122 Ceyrat - FRANCE

Professor B. L. SHAPIRO
966 Elsinor Court
Palo Alto
California 94303 - Etats Unis

Dear Dr Shapiro

Theix, 1994 junuary 31
(received 2/7/94)

STUDY OF THE WATER DIFFUSION COEFFICIENT IN COLLAGEN FIBERS BY ^1H NMR

To measure the anisotropic behaviour of the water diffusion coefficient in oriented hydrated-collagen fibers, two pulse sequences were used and compared. With **P**ulse **G**radient **S**timulated **E**cho (*PG-STE*)[1]method, D is measured from the extent of signal attenuation as a function of the strength of a pair of magnetic field gradient pulses (Fig. 1), while with the **O**ne **E**cho -**C**onstant-**T**ime, **P**ulse, and -**G**radient -amplitude (*OE-CTPG*)[2] method, the magnetic field gradient pulse and the length of the echo sequence are constant and hence D is obtained from the attenuation of the echo amplitude as the function of time (Fig. 2).

All experiments were performed at 25°C on a Bruker AM400 spectrometer equipped with the micro imaging accessory. For the *PG-STE* method, the gradients varied from 0.5 to 10 Gauss/cm in increments of 0.5. For *OE-CTPG*, a gradient of 2 Gauss/cm was used. Hydrated-collagen samples were placed in a solenoid coil with the principal fiber axis in a position perpendicular to the static magnetic field B_0.

The two methods showed the isotropic behaviour of D in pure water and the values (around $2.3*10^{-5}$ cm^2/s) were similar to those in the literature. For hydrated collagen, all experiments showed a decrease of D in all directions. The results from *PG-STE* experiment showed a similar behaviour of Dx (along the fiber axis) and Dz (across the fiber axis). With the *OE-CTPG* method, Dy and Dz were alike and Dx was greater than Dy and Dz. The last measurement was in agreement with the position of the sample in the probe. The restricted behaviour of diffusion was shown by the change in D as a function of echo time. With *PG-STE* method, as many echo times as experiments were performed while the *OE-CTPG* method needed only one experiment (Fig. 3). These results show that the *OE-CTPG* method is suitable for measuring restricted diffusion in oriented collagen fibers.

Sincerely yours

A. TRAORE L. FOUCAT J.P. RENOU

	PG-STE			*OE-CTPG*		
Sample	Dx	Dy	Dz	Dx	Dy	Dz
Pure water	2.27	2.41	2.30	2.33	2.36	2.32
Hydrated collagen	1.44	0.70	1.38	1.23	0.69	0,74

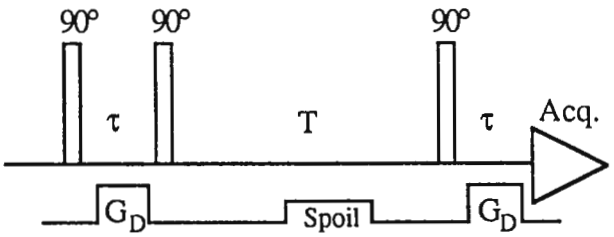

Fig.1 : *PG-STE* sequence

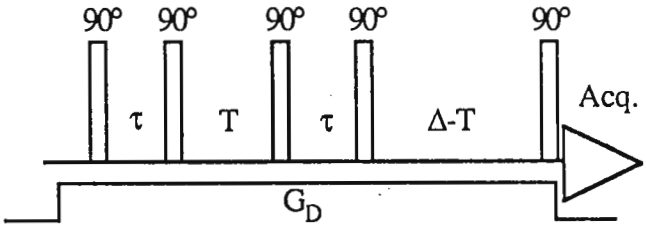

Fig.2 : *OE-CTPG* sequence

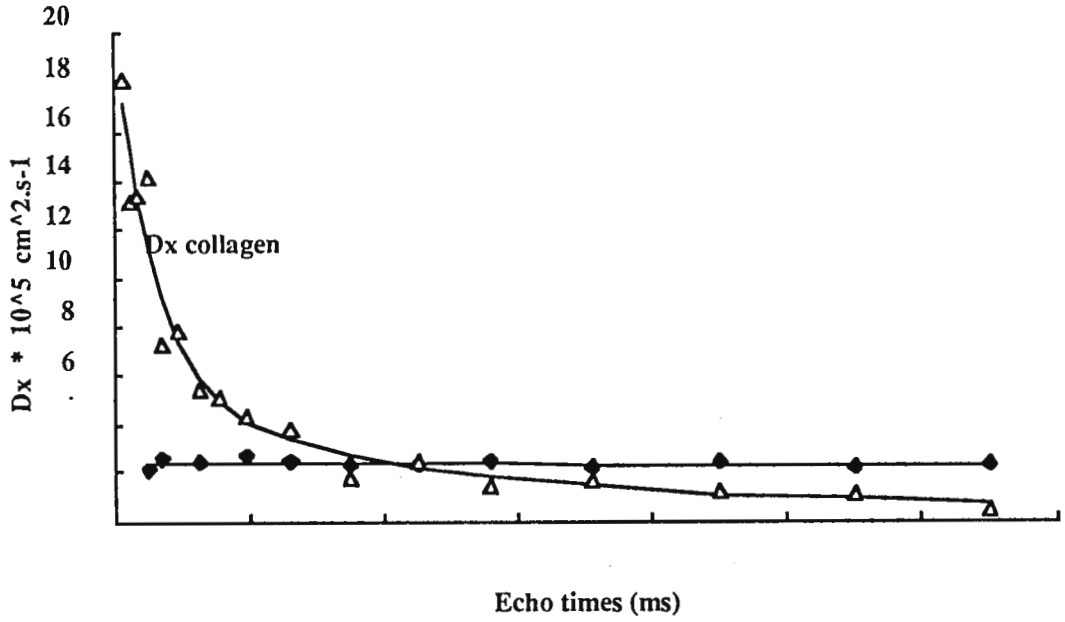

Fig.3 : Dx as a function of echo time from *OE-CTPG*.

1- T. J. Norwood, J. Magn. Reson., A **103**, 258-267 (1993).

2 - J. E. Tanner, J. Chem. Phys., **52**, 2523-2526 (1970).

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February 1, 1994
(received 2/4/94)

Dr. Barry Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

RE: Restricted Motions in PFG Diffusion Experiments

Dear Dr. Shapiro

At Staley we are now using our pulsed field gradient equipment and routinely apply gradients of 150 Gauss/cm. We are using Dr. Charles Johnson's LED sequence to minimize eddy current effects. However, we found that "starch solutions" do not always exhibit the classical exponential decay in diffusion experiments, i.e., plotting M/M_0 (Ψ) *vs* g does not fit $\Psi = \exp(- (\gamma\delta g)^2 D (\Delta - \delta/3))$.[1] In addition, decay curves do not depend on the diffusion time, Δ. Therefore, the motion of the polyglucoside must be restricted.

Our decay curves do not seem to fit the mathematical models in the literature, but do match a simple parabolic function quite well: $\Psi = 1 - (\gamma\delta g R)^2$. Although this relation is entirely empirical, we hope that R has a similar meaning as that in the other models. R, which is in units of centimeters, should give us a measure of the "movement range" in our studies of starch solutions.

Sincerely,

Gary Juneau

Gary Juneau

1. Karger, J., Pfiefer, H., Heink, W.,"Principles and Applications of Self Diffusion Measurements by Nuclear Magnetic Resonance," Advances in Magnetic Resonance, Vol 12, (1988)

skd:h:\tamu2

T · H · E
OHIO STATE UNIVERSITY

Department of Chemistry
Professor Gideon Fraenkel

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(received 1/31/94)

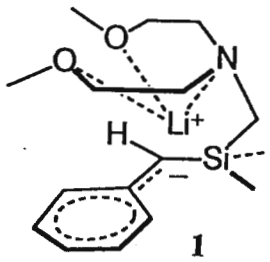
Dr. B.L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

January 19, 1994
Detectable covalency C,Li bond in a benzyllithium

Dear Barry:

Salar spin coupling, between ^{13}C and directly bonded ^{6}Li (^{7}Li relaxes too fast) is a well documented feature of the NMR of numerous organolithium compounds. Surprisingly much of the data fall into a simple pattern, that $^{1}J(^{13}C,^{6}Li) \sim 16/n$ Hz where n is the state of aggregation; apparently there is little dependence on the structure of the organic moiety of (RLi)n. In general, the species which don't exhibit this coupling are the ones believed to consist of ion-pairs which contain delocalized carbanions, the latter inferred from the carbon shifts. Thus, it has been rationalized that one would expect minimum C, Li convalency or if there is covalency, these "bonds" would have minimum associated "s" character. Carbon, lithium coupling in such species might also be averaged as a result of interaggregate C, Li bond exchange, still fast at 150K, below which temperature most of these samples freeze.

One might think there should be a continuum of ^{13}C, ^{6}Li, coupling constants between those 16/n Hz values described above and those for which the coupling is too small to observe. Just lately we have a missing link, species **1** in **THF-D_8**. From the non equivalence of pendant ligand and silymethyl carbons we conclude the compound exists in the folded structure shown. Furthermore, below 240K there is a well resolved ^{13}C (benzyl), ^{6}Li coupling of 2.8 Hz (7.4 Hz, as expected, for the ^{7}Li species). The carbon analog of **1**(C for Si) shows a broad benzyl ^{13}C resonance which sharpens up on irradiating at the ^{6}Li resonance, hence detectable coupling between benzyl ^{13}C and ^{6}Li. This implies that in both compounds there is detectable C, Li covalency with some associated "s" character. We see this because intermolecular C, Li bond exchange is slow due to the encapsulated site of lithium. The conclusions drawn here probably apply to all benzyllithiums in most of which C, Li bond exchange is fast enough to average the carbon lithium coupling. Small distortions of coplanarity of substituents on benzyl carbon with the phenyl moiety in benzyllithiums have been observed crystallographically.



1

Above 240K with increasing temperature, the ^{13}C, ^{6}Li coupling in **1** is progressively averaged due to intermolecular C, Li exchange. Line-shape analysis yields $\Delta H^{\neq} = 5.5$ kcal/mole and $\Delta S^{\neq} = -35$ eu.

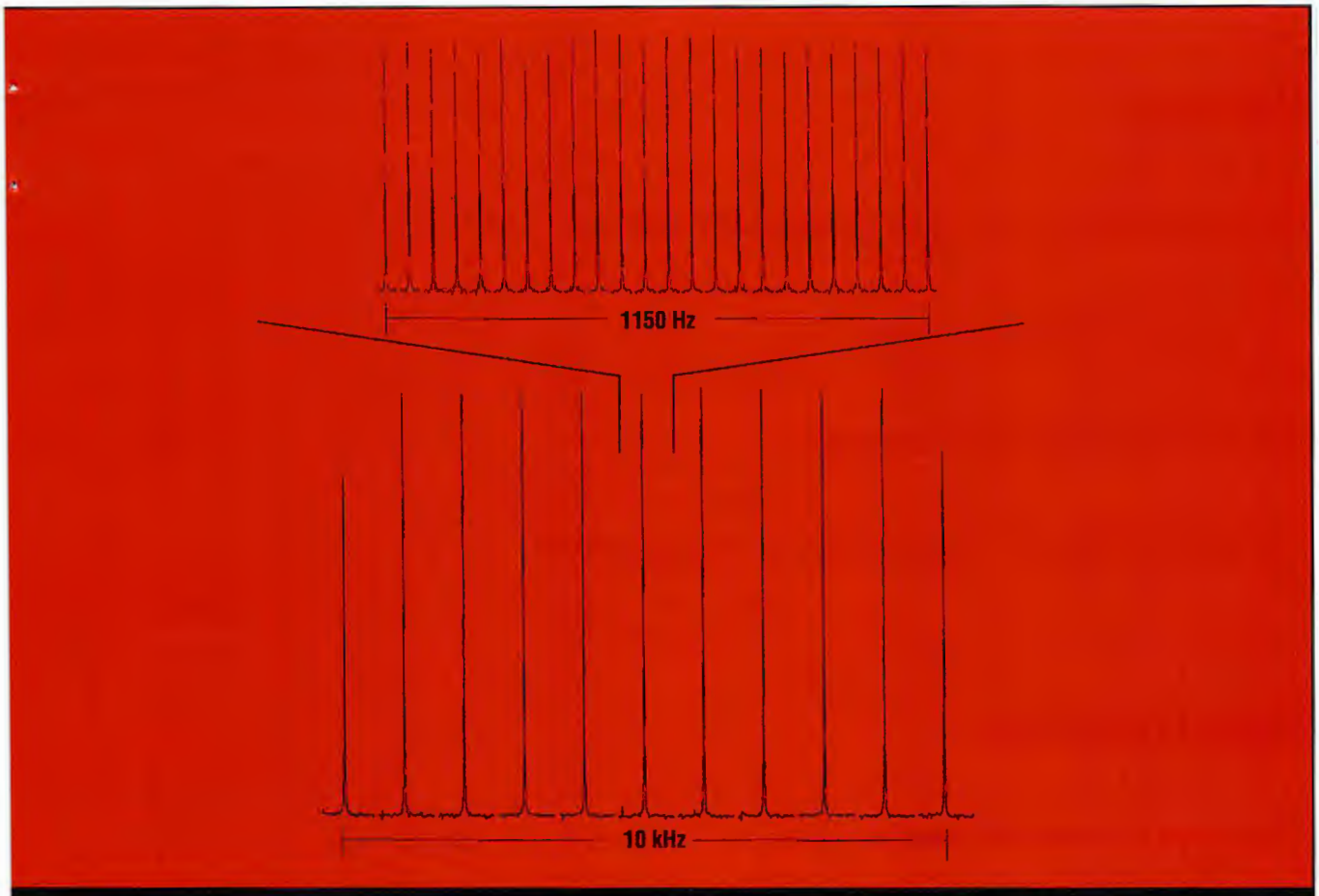
Our very best regards to you and the NMR community for a productive 1994.

Your sincerely,

Gideon Fraenkel
Professor

Kevin Martin
Research Assistant

Maintain Deuterium Lock During Deuterium Decoupling



This array of deuterium-decoupled ^{13}C spectra of deuterobenzene was obtained on a UNITYplus 500 with a Triple•nmr Pulsed Field Gradient probe, locked on deuterium in C_6D_6, using the UNITYplus Adaptive Lock. The GARP-modulated deuterium decoupling offset was changed in 1000 Hz steps for the lower array and 50 Hz steps in the upper array. The 1150 Hz deuterium decoupling bandwidth (>15 ppm) demonstrated in the upper spectral array was achieved using only 1 watt of decoupling power applied to the lock channel of the probe.

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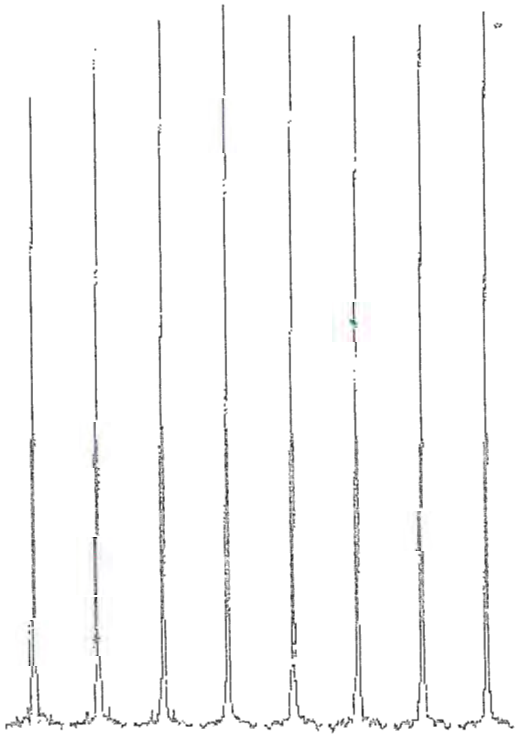

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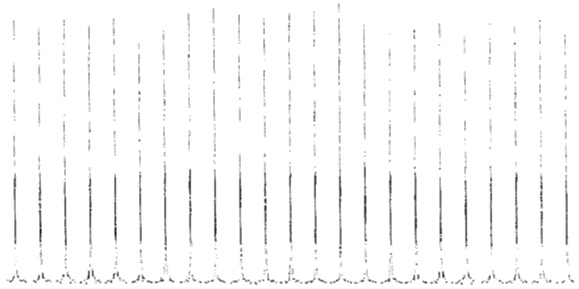

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February 10, 1994
(received 2/17/94)

^{15}N and ^{13}C CHEMICAL SHIFT CALIBRATION

Dear Barry:

Having essentially completed the installation and testing phase of our new NMR laboratory, I decided to revisit the issue of ^{15}N chemical shift referencing applying the approach we (JACS V.106, p. 1939, 1984) and others have used based on the knowledge of the ^{1}H reference position. The point of this method, which is general to other nuclei, is to get accurate chemical shifts for heteronuclei, particularly in multidimensional experiments, while avoiding the complication of using internal shift standards for heteronuclei. To do this for ^{15}N, a standard sample containing ^{1}H and ^{15}N standards, in this case TMS and CH_3NO_2, was run. From the 1D spectra for each of the nuclei the absolute frequency of TMS is measured and that of NH_3 is deduced using the literature value of -381.9 for the shift of NH_3 relative to nitromethane. With these numbers and their calculated ratio the 0 reference position for ^{15}N can be determined in any sample. This can be done in one of two ways. The first is to take the absolute frequency of the 0 position from the standard sample and add to it the product of the ratio of the ^{15}N and ^{1}H frequencies in the standard times the difference between absolute frequency of TMS in the standard sample and the frequency of the 0 ^{1}H position in the sample currently under study. This works well if the standard frequencies are available for a spectrometer at the same or very similar field to what you are running. Alternatively, one can multiply the absolute frequency of the ^{1}H 0 position in the sample in question by the ratio determined in the standard sample to a sufficient number of places, typically 9, to get the ^{15}N reference. In my experience, arithmetic errors in the first approach are more obvious since you are always comparing to the standard value, and I have tended to use it to be safe. The sample in the original report contained CH_3NO_2 and TMS in $CDCl_3$ as a lock. I recently became aware of a solvent effect of chloroform on the shift of nitromethane. In order to minimize this perturbation, and taking advantage of more sensitive locks, I repeated the experiment now using a 90% solution of CH_3NO_2 in acetone with a small amount of TMS. The solvent effect of acetone is much lower than for chloroform, and its proportion was kept to a minimum. The results of the new and more accurate calibrations on a 500 and a 600 MHz spectrometer are given below.

TMS = 598,956,768.3 Hz NH_3 = 60,691,668.3 ratio = 0.101328963

TMS = 499,891,209.9 Hz NH_3 = 50,653,456.1 ratio = 0.101328959

Because of the increased interest in making accurate determination of ^{13}C shifts for use in assignment of proteins, measurements have also been made for ^{13}C. At the suggestion of Ad Bax, I have checked both TMS and DSS since different groups may use either one. For TMS in $CDCl_3$ and DSS (or TSP) in D_2O results are

TMS = 598,956,787.2 TMS_C = 150,607,677.4 ratio = 0.2514499887

TMS = 499,891,225.1 TMS_C = 125,697,641.5 ratio = 0.2514499859

DSS = 499,889,884.0 DSS_C = 125,697,083.5 ratio = 0.2514495442

Thus ^{13}C shifts referred to DSS will be 1.75 ppm greater than those referenced to TMS. All measurements were made at 30 C. The ratio for DSS is in very good agreement with the one reported by Bax and Subramanian (JMR, V.67, p.565, 1986) of 0.25144954.

Sincerely yours,

David Live

New NMR Positions (summer, 1994)

The NMR laboratory of the Biotechnology Research Institute (BRI) is seeking research associates or postdoctoral fellows to join our research team to characterize the solution structure, dynamics and interactions of blood coagulation and signal transduction proteins by NMR spectroscopy. These positions will be supported jointly by BRI and by an MRC (Medical Research Council Canada) grant and will be initially for two years and extendable thereafter depending on the funding situation. The successful candidates will work closely with molecular biologists and protein chemists at BRI. Our laboratory is equipped with two Brüker (AM-500 and AMX-500) NMR spectrometers. We also have access to a Brüker AMX-600 spectrometer located in the NRC laboratories in Ottawa. These instruments are connected to a network of Silicon Graphics workstations for data processing and molecular modelling. Interested candidates should contact Dr. Feng Ni at:

Phone: (514)-496-6729; Fax: (514)-496-5143
e_mail: fengni@bobino.bri.nrc.ca

or send a CV and 2 letters of reference to:

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Pulse width	10 ms	20 ms
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(AMPX00HV) 02/94

LOUISIANA STATE UNIVERSITY
AND AGRICULTURAL AND MECHANICAL COLLEGE
Department of Chemistry

Dr. B. L. Shapiro, Editor
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94393

February 1, 1994
(received 2/5/94)

^{27}Al NMR at 4.2 K and a Spectral Width of 7 MHz

Dear Dr. Shapiro:

A field swept NMR spectrometer has been constructed here in LSU, based on a 16 /18 Tesla (4.2 /2 K operation) superconducting magnet, the largest field yet used for field swept NMR. We have successfully acquired several ^{27}Al powder patterns (Figure 1, 2) with a field-swept pulsed NMR technique.

The ^{27}Al NMR spectra shown in Figure 1 are our first results performed in a magnetic field swept mode at 4.2 K. Each data point in the spectrum corresponds to the integrated free-induction decay following a 100 μs, small tip angle pulse. The experiment has a high signal-to-noise ratio. Figure 1b shows that satisfactory results can even be obtained when operating with an improperly tuned probe.

In principle, it should be possible to obtain reliable multiparameter fits for complex line shapes arising from overlapping spectra of multiple sites. Therefore, the second test sample chosen is andalusite crystal which has large ^{27}Al quadrupole coupling constants (C_Q) and two ^{27}Al sites. The top trace in Figure 2 is the ^{27}Al spectrum when the crystal is mounted with crystal face (001) perpendicular to the magnetic field. The bottom trace in Figure 2 is the simulation based on complete powder pattern simulation at each magnetic field point. The two ^{27}Al sites have a population ratio of 1:1 with C_Q = 15.6 MHz η = 0.08 and C_Q = 5.9 MHz, η = 0.8 respectively. Interestingly, we seemed to have uncovered a low temperature phase transition. Preliminary variable temperature ^{27}Al NMR work indicate the phase transition occurs near 75 K.

We find that the experiment is relatively easy to perform and the operation at 4.2 K largely eliminates the resulting motional averaging of the electric field gradient at the quadrupole nucleus site. This experimental condition can be advantageous for many cases.

In summary, this instrument provides a means of acquiring high-quality solid-state NMR spectra for materials containing difficult nuclei such as ^{27}Al, ^{91}Zr, ^{23}Na, ^{11}B, and ^{93}Nb for which large quadrupole coupling constants are common.

Sincerely,

Xiao Wu

Leslie G. Butler

Baton Rouge • Louisiana • 70803-1804 • 504/388-3361 • FAX 504/388-3458

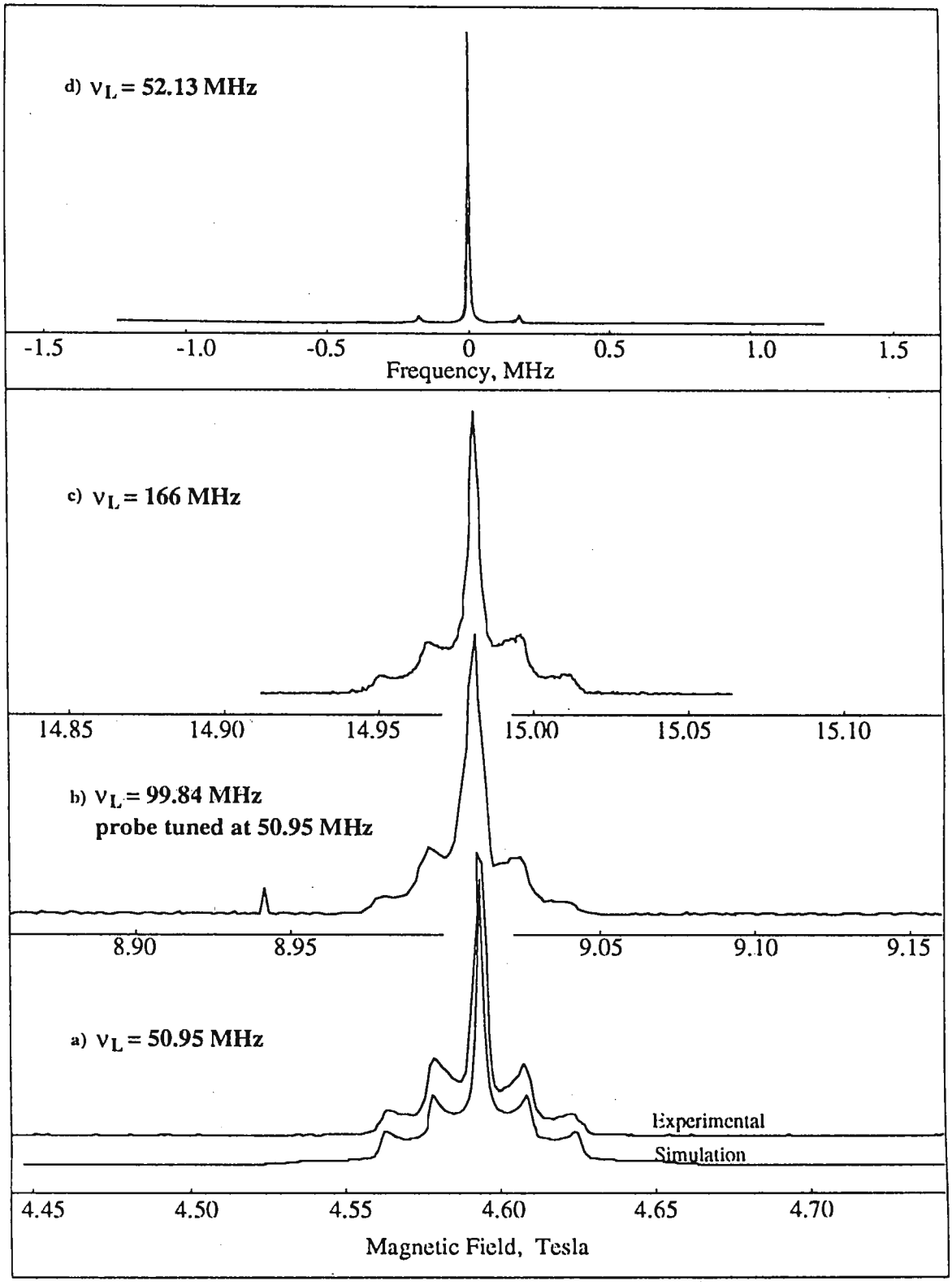

Figure 1: Magnetic field swept ^{27}Al NMR spectra of alumina α-alumina at 4.2 K and three different RF carrier frequencies. (a) Each data point in the spectrum is the average of magnitude values from four FIDs and the entire spectrum was acquired in 2.5 hours. The simulated line shape is corrected for magnetic field sweep effects and is based on a quadrupole coupling constant of 2.33 MHz and an asymmetry parameter of zero. (b) For this run, the probe was left tuned to 50.95 MHz; in spite of mistuning, an adequate spectrum is obtained. (c) Carrier frequency is 166 MHz, a smaller sample used. (d) This spectrum acquired with a conventional solid-state NMR spectrometer operating at 4.7 T (Bruker MSL200), 300 K, and using a 1 μs RF pulse. Average of 200 transients.

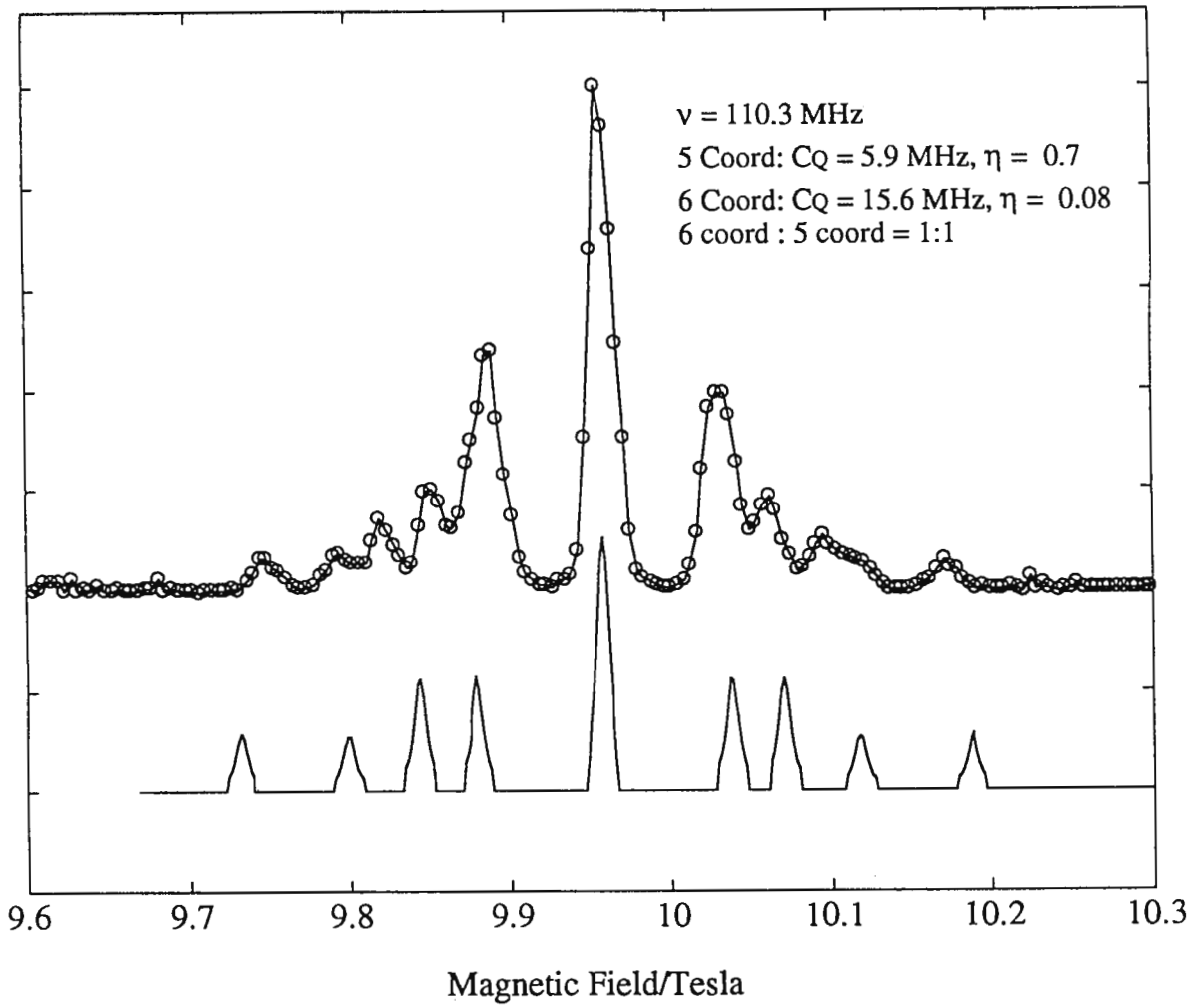

Figure 2: ^{27}Al spectra of an andalusite single crystal. The spectrum was acquired with spin echo pulse sequence. The top trace is experimental data; the bottom trace is simulation. Extra peaks tentatively attributed to a phase transition that occurs near 75 K.

FORTHCOMING NMR MEETINGS, *Continued from page 1.*

XVIth International Conference on Magnetic Resonance in Biological Systems, Veldhoven, The Netherlands, **August 14 - 19, 1994**; Organizing Committee: M. J. A. de Bie, C. W. Hilbers, R. Kaptein; Contact: Secretariat XVIth ICMRBS, Bijvoet Center for Biolmolecular Research, Padualaan 8, NL-3584 CH Utrecht, The Netherlands; Tel. +31 30 53 2652/2184/3801; Fax: +31 30 53 7623/54 0980.

Ampere Summer School on Magnetic Resonance with Spatial Resolution, Eichstätt, Bavaria, Germany, **September 2 - 8, 1994**; Contact: L. D. Hall or B. Blümich - See TAMU NMR Newsletter 426, 56.

Symposium on "NMR as a Structural Tool for Macromolecules: Current Status and Future Directions, Indianapolis, IN, **October 30 - November 1, 1994**; Contact: Ms. Padmini Nallana, Coordinator, NMR Symposium, Dept. of Physics, Indiana University Purdue University Indianapolis, 402 N. Blackford St., Indianapolis, IN 46202-3273; Tel. (317) 278-1263; E-mail: PADMINI@INDYVAX.IUPUI.EDU; Fax: (3172) 274-2393. See TAMU NMR Newsletter 425, 31.

36th ENC (Experimental NMR Conference), Boston, MA, **March 26 - 30, 1995**; Contact: ENC, 815 Don Gaspar, Santa Fe, NM 87501; (505) 989-4573; Fax: (505) 989-1073

12th International Meeting on NMR Spectroscopy, Sponsored by the Royal Society of Chemistry, Manchester, England, **July 2 - 7, 1995** [sic]; Contact: Dr. J. F. Gibson or Ms. G. B. Howlett - See TAMU NMR Newsletter 415, 5; Phone: (44-71) 437-8656; Fax: (44-71) 437-8883.

ISMAR 1995, Sydney, NSW, Australia, **July 16-21, 1995**; Contact: Dr. Les. Field, Dept. of Organic Chemistry, Univ. of Sydney, Sydney, NSW 2006, Australia. Phone: +61-2-692-2060; Fax: +61-2-692-3329; Email: ismar-95@biochem.su.oz.au Also, see TAMU NMR Newsletter 419, 26.

Additional listings of meetings, etc., are invited.

Department of Medicinal Chemistry
Central Research Division
Pfizer Inc
Eastern Point Road
Groton, CT 06340

Central Research
NMR Spectroscopy

January 31, 1994
(received 2/4/94)

Dr. Barry Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

...Probes by Any Other Name...

Dear Dr. Shapiro,

We were recently in a position to buy a second probe for our Bruker AMX-600 three channel spectrometer, and chose to evaluate (and subsequently buy) the 5 mm triple resonance inverse probe offered by Nalorac Cryogenics Corporation. We were quite satisfied with the performance of this probe, and would like to compare and contrast this probe with our original Bruker 5 mm triple resonance inverse probe.

Quantitative factors. We spend most of our time in water, so lineshape and sensitivity are pretty important. Below is a summary of numbers one typically examines when evaluating probe performance:

Measurement	*Nalorac*	*Bruker*
Sensitivity (ethyl benzene)	787:1 (front loaded)	
	680:1 (standard)	564:1 (standard)
proton 90°	5.8 us (front loaded)	
	6.9 us	7.4 us
carbon 90°	13.5 us	13 us
nitrogen 90°	35 us	35 us
Spinning lineshape (chloroform)	3 / 6 (Hz)	4 / 8 (Hz)
Non-spinning lineshape (chloroform)	5 / 10 (Hz)	5 / 10 (Hz)
Water suppression (sucrose std.)	60 / 120 (Hz)	80 / 140 (Hz)

Most of these experiments are standard ones, except the water suppression experiment is a measure of the width of the water at 50% and 20% the height of the DSS. All numbers were obtained by us on a routine basis without prior tweaking except for the chloroform numbers, which were measured by instrument engineers.

Qualitative factors. The Bruker probe responds much better to the temperature control system. The Nalorac probe was not designed to accommodate the BTO-2000 thermocouple (on this thermocouple, however, water freezes at 277.5 K). The Nalorac probe is slower to reach temperature, but is equally stable once the desired temperature is reached. The Nalorac probe also has a longer coil, making it necessary to use slightly larger samples (we have observed ~10% better S/N for this probe over the Bruker probe when identical samples are used (0.5-0.6ml), but they are harder to shim). The Nalorac probe is, in our hands, much easier to optimize for 1,-1 excitation and produces a much better null.

Overall. Both probes are excellent for work in water where high sensitivity is required. I would expect that probe-to-probe differences are greater than vendor differences in this area.

Sincerely,

Walt

Walter Massefski, Jr.

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82-00808-7	Dimethyl-d_6 Sulfone	98 atom%
82-04043-7	Ethylene-1,1-d_2	98 atom%
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March 1, 1994
(received 2/17/94)

Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Methomyl Metabolite Structure Assignment by HMBC

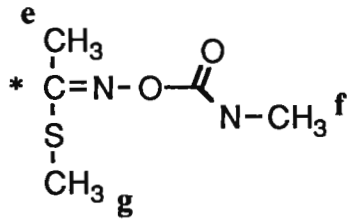
Dear Dr. Shapiro,

A large portion of our spectrometer time is spent looking at xenobiotic conjugates of agrochemicals. Difficulty arises in these studies due to the small mass of sample available, and the general purity of compounds submitted.

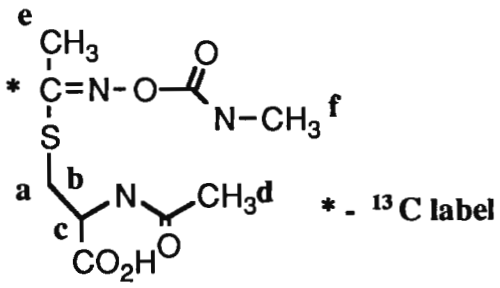
In order to assist Mass Spectral interpretation, a combination of ^{14}C, ^{13}C, and unlabeled test substances are sometimes used. In these cases, experiments are performed using an approximate 1:1 ratio of ^{13}C labeled and unlabeled test substance. The use of this mixture ensures that the isolated metabolites generate a doublet of ions of equal intensity in the mass spectrum, thereby differentiating compounds of interest from unlabeled contaminants.

Recently, we have taken advantage of the dual isotope labeling to obtain information about a metabolite of Methomyl through NMR. The isolated metabolite (50 µg) was dissolved in 0.5 ml D_2O. Data were acquired using a Bruker AMX-360 equipped with a 5 mm inverse probe.

Using Heteronuclear Multiple Bond Correlation (HMBC), we were able to establish long range coupling from the conjugate to the ^{13}C label of the parent compound. The presence of only a single labeled site in these studies allows for specific conjugation mechanism information. This, along with information provided by DQF-COSY, gives the assignment of structure indicated below:



Methomyl



Methomyl Metabolite

The 50% ^{13}C label gives a characteristic "triplet" for each of the methyls **e** and **g** in the 1D 1H spectrum of the parent at 2.3 δ and 2.5 δ, respectively. The "triplet" is actually the superposition of two chemical shifts for the protons coupled to the label and those that are not. The set of resonances due to **g** are missing from the spectrum of the metabolite. Protons **a** and **b** on the metabolite would normally be doublets of doublets, but are not distinguishable as such due to additional coupling to the label. DQF-COSY data (Fig. 1) shows that protons **a**, **b**, and **c** are coupled and may be assigned as the cysteinyl portion of the metabolite. Methyl groups **d**, **e**, and **f** are resonant at 2.05 δ, 2.33 δ, and 2.8 δ, respectively. HMBC data (Fig. 2) indicates coupling between the labeled carbon (165 δ) and protons on the methyl group **e**, as well as protons **a** and **b** on the cysteinyl methylene.

Respectfully submitted,

Bill Payne

Dave Ryan

Please credit this contribution to the account of Patricia L. Watson.

Figure 1

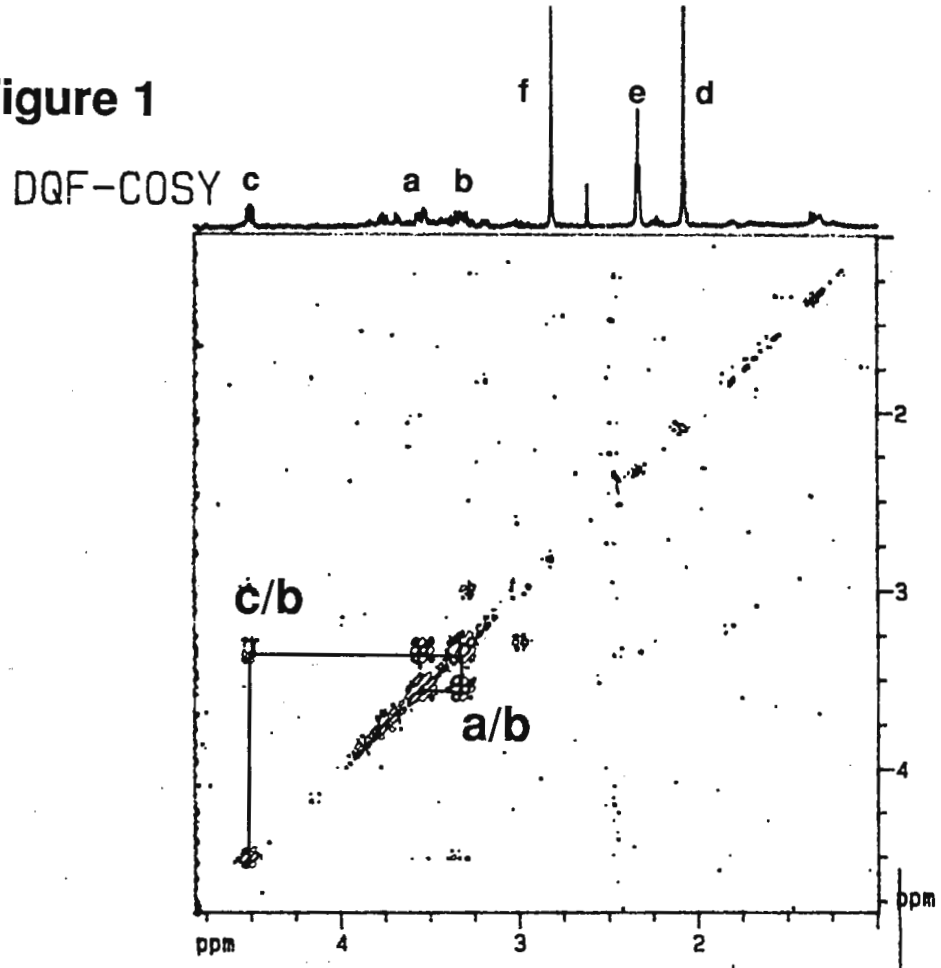
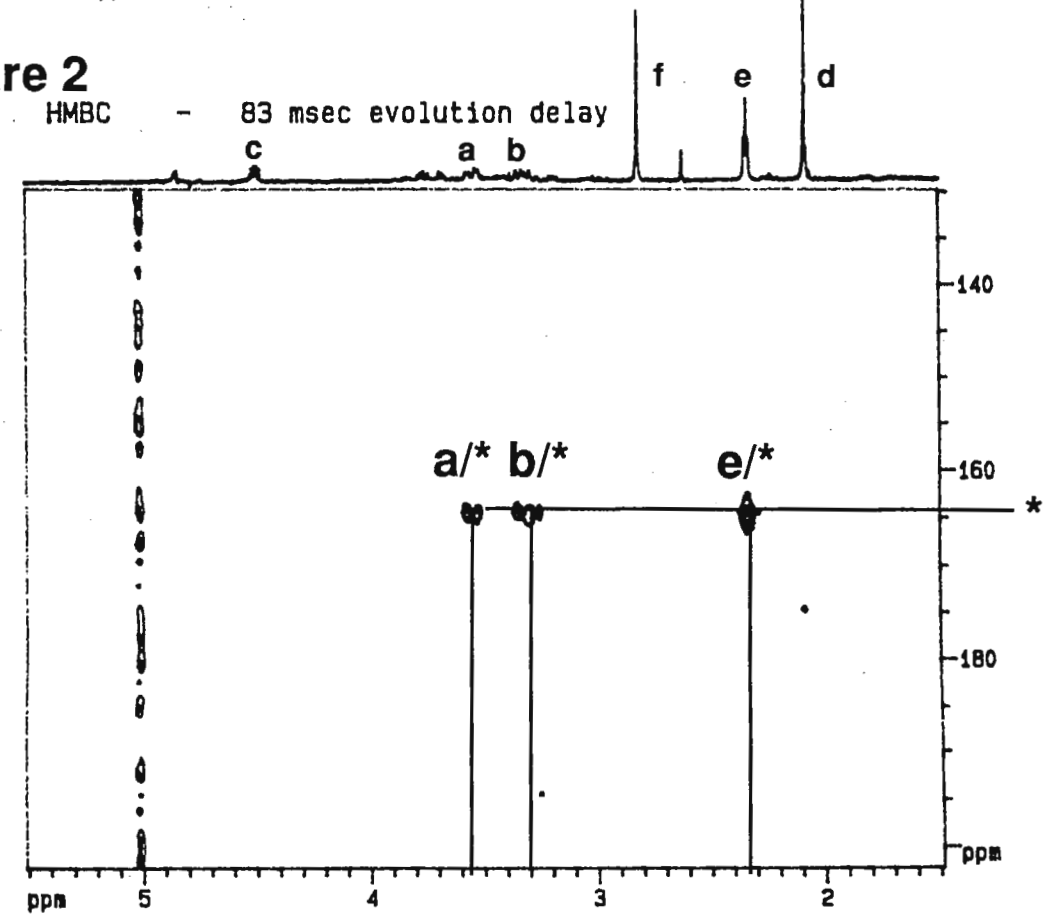


Figure 2



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^{139}La Nuclear Quadrupole Coupling in La_2O_3

(received 2/18/94)

Dear Dr Shapiro,

We have recently been making ^{139}La NMR measurements of quadrupole coupling constants and transferred magnetic hyperfine interactions in La_2O_3 and a series of perovskites $La_{1-x}Sr_xMO_3$ (where M=Cr, Mn, Co). Depending on the doping level of SrO_2 these materials are either paramagnetic or ferromagnetic at room temperature. The full results will appear in due course in Solid State Nuclear Magnetic Resonance. In the mean time your readers might be interested in the results for La_2O_3

The ^{139}La spectra were obtained at room temperature on a Bruker MSL 400 spectrometer using a nominal field of 9.4 T. The resonances were located by searching in relatively coarse steps (ca. 100kHz to 1MHz), starting from the resonance frequency for the diamagnetic ion, and using the echo sequence: $\theta_1 - \tau - \theta_2 - \tau$ - acq, with $\theta_1 = 5\mu s$ and $\theta_2 = 10\mu s$. The frequency was then incremented in suitably small steps and the line-shape traced out by measuring the height of the Fourier transformed spin-echo at the current operating frequency. The NQR spectrum of La_2O_3 was obtained by conventional pulsed Fourier transform spectroscopy, with the NMR probe in zero field. The ^{139}La reference frequency was derived from an aqueous solution of $La(NO_3)_3.6H_2O$ which yielded a sharp line at 56.5236 MHz. The ^{139}La NMR spectra exhibited in Figs 1(a) and (b) are plotted with the frequency axis indicating the offset from 56.500 MHz.

The structure of La_2O_3 is hexagonal, space group C3m, with one lanthanum atom and two distinguishable oxygen atoms per unit cell [1]. A previous ^{17}O MAS NMR study [2] has shown the two oxygen sites as two well resolved resonances with intensity ratio 1:2, consistent with crystal structure [1]. The lanthanum site has axial symmetry so that the ^{139}La quadrupole interaction has $\eta = 0$, as indicated by the NMR spectrum in Fig 1a. The value of the coupling constant C_q (= e^2qQ/h) was consistently determined in three ways in order of increasing accuracy: from the second order perturbed (-1/2,1/2) NMR lineshape shown in Fig 1a, from the separation of the (1/2,3/2) and (-3/2,-1/2) $\theta=\pi/2$ satellite singularities (Fig 1b), and finally, in zero magnetic field, from the centre frequency of the (±7/2,±5/2) NQR transition (Fig 2). Since the first two methods require allowance for an amount of dipolar broadening, which is not precisely known, they are intrinsically less accurate than the third method, which yielded a value $3C_q/14 = 12.54$ MHz, ie. $C_q = 58.52$ MHz at 294 K.

1. R.Wyckoff, "Crystal Structures", 2nd ed., Wiley, New York 1964, Vol.2, p.1.
2. T.J.Bastow and S.N.Stuart, Chem.Phys., **143**, 459 (1990).

Please credit this contribution to Professor I.D.Rae's subscription.
Best wishes,

T.J.Bastow

Fig 1.

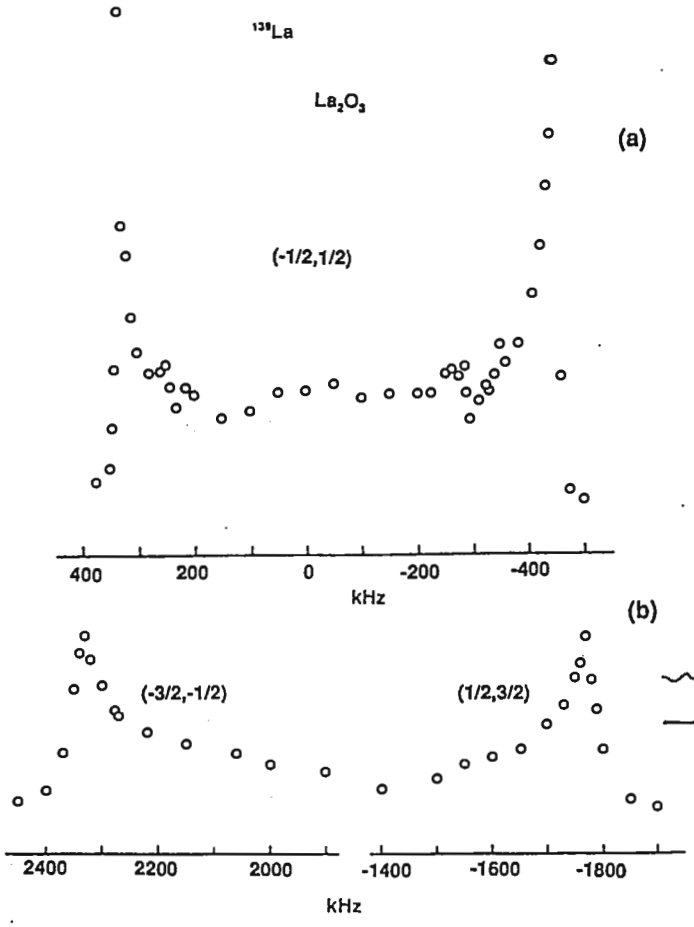

Fig 2.

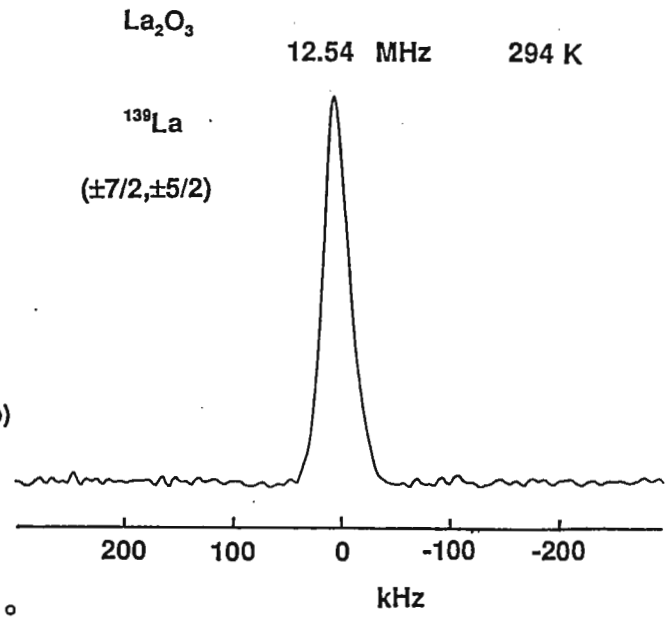

Fig 1. ^{139}La NMR spectrum of polycrystalline La_2O_3; (a) (-1/2,1/2) and (b) (-3/2,-1/2) and (1/2,3/2) transition.

Fig 2. ^{139}La (±7/2,±5/2) NQR transition for La_2O_3. The zero of the frequency scale corresponds to the spectrometer frequency of 12.53 MHz.

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Electrical

Description/Application

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Co-developer

Centre for Magnetic Resonance, University of Queensland
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Benefits Gained from this Development

Higher quality images. Compared with adhesive lamination, use of plated TEFLON reduces the potential for gaps and eliminates the need for adhesives, both of which would decrease reception sensitivity and increase background noise, according to Polyflon.

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Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto California, 94303

February 1, 1994
(received 1/31/94)

Complete Carbon-13 Chemical Shift Tensors in Carbohydrates

Dear Dr. Barry Shapiro,

We have been studying carbon-13 chemical shift tensors in sugars containing only carbon, oxygen and hydrogen atoms linked by single bonds. These shift tensors depend on both the configuration and conformation of the molecule. In order to obtain the orientation of the chemical shift tensor relative to a fixed molecule, single crystal studies are necessary. A 2D chemical shift tensor measurement technique has been applied to measure the complete carbon-13 chemical shift tensors in the following carbohydrates: methyl-α-D-galactopyranoside, methyl-α-D-glucopyranoside, methyl-α-D-mannopyranoside, methyl-β-D-galactopyranoside, methyl-β-D-glucopyranoside, and methyl-β-D-xylopyranoside.

In these carbohydrate molecules, principal axes of carbon chemical shifts mostly depend on local symmetry of the molecule. For each carbon nucleus in the molecule, a *pseudo* principal axes can be defined based on the immediate configuration of the carbon atom. The chemical shifts along these directions can be calculated with NMR experimental data. Those corresponding most closely to the principal values are assigned. In addition, Gauge-Invariant Atomic Orbital (GIAO) calculations have been also applied to all the molecules studied. By comparing the experimental data to GIAO calculations with all possible permutations, the permutation which yields the minimum sum of squares of deviations of icosahedral shifts is chosen as the best assignment. The chemical shifts can be correlated with a scatter of 3.0 ppm by GIAO calculations using the 3-21G basis set.

The chemical shift data for methyl-α-D-galactopyranoside and methyl-β-D-galactopyranoside are given below. The experimental data show that the chemical shifts are not solely determined by the configuration of the directly bonded atoms, but that they depend on the configuration and conformation of the molecule as a whole.

Chemical Shift Principal Values for methyl-α-D-galactopyranoside and methyl-β-D-galactopyranoside (in parentheses)

	δ_{11}	δ_{22}	δ_{33}	δ_{ISO}
C1	118.5(118.7)	96.5(105.3)	86.3(92.8)	100.4(105.6)
C2	89.1(88.8)	67.5(72.1)	46.3(52.9)	67.6(71.3)
C3	94.9(90.0)	71.9(76.4)	50.9(50.1)	72.6(72.2)
C4	88.2(89.0)	67.9(69.5)	54.0(49.4)	70.0(69.3)
C5	93.9(92.7)	69.4(80.9)	55.5(52.7)	72.9(75.5)
C6	86.6(89.6)	68.0(69.7)	29.4(30.0)	61.4(63.1)
C7	88.8(94.2)	72.7(75.4)	4.0(3.9)	55.2(57.8)

Best Regards,

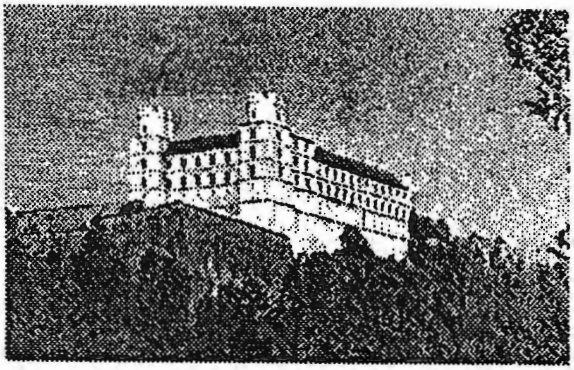
Fang Liu

Donald W. Alderman

David M. Grant

Department of Chemistry
Henry Eyring Building
Salt Lake City, Utah 84112

Ampere Summer School on Magnetic Resonance with Spatial Resolution



Organized by the Division of Spatially Resolved Magnetic Resonance of the Ampere Society

Sept. 2 to 8, 1994
Eichstätt, Bavaria, Germany

Program:

The program consists of sessions with lectures and tutorials. Each afternoon will provide ample time for special activities and discussions of detailed topics. The following topics will be covered:

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- imaging sequences
- quantitative imaging
- fast imaging
- spectroscopy
- susceptibility
- microscopy
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- diffusion and perfusion
- imaging of solids
- contrast agents
- medical imaging
- animal imaging
- plants
- food
- porous media
- polymers

Lecturers:

The lectures are given by the following scientists:

E. R. Andrew, Gainesville
B. Blümich, Aachen
P. T. Callaghan, Palmerston North
T. A. Carpenter, Cambridge
A. Haase, Würzburg
L. D. Hall, Cambridge
G. A. Johnson, Durham, NC
W. Kuhn, St. Ingbert
G. J. Nesbitt, Amsterdam

Conference Material:

The lectures will be based on the book *Principles of Nuclear Magnetic Resonance Microscopy*, Clarendon Press, Oxford, 1991. One copy of the book is included in the registration fee.

Participation and Registration:

The number of participants is limited to 50. The conference fee is SFr 1500.-- (Swiss Francs) for regular participants and SFr 900.-- for students. It includes room and board with breakfast and dinner, no lunch. Arrival is Sept. 2 in the afternoon, departure is on Sept. 8 at noon.

For registration please fill in the attached form. The deadline is **May 31st, 1994.**

Scientific Program:

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600 N. WOLFE STREET,
BALTIMORE, MD 21287

Professor B.L. Shapiro,
TAMU NMR Newsletter,
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Palo Alto, CA 94303

February 4, 1994
(received 2/13/94)

PROTON SPECTROSCOPIC IMAGING OF HUMAN STROKE

Dear Professor Shapiro,

Thank you for your recent "ultimatum". Over the past year and a quarter we have been using the recently developed technique of multi-slice proton spectroscopic imaging (1) to investigate cerebral metabolite levels in a number of different patient pathologies. The sequence, developed by the group at the *In Vivo* NMR Center at the National Institutes of Health, runs on a standard GE Signa scanner operating the 4.8 version software and proton spectroscopy accessory package.

One of the most promising clinical applications of this method is in the diagnosis of patients with ischemic brain disease. It has been previously noted (2) that conventional MR imaging is often unable to detect ischemic brain regions in the acute stage of the disease, and is also often unable to distinguish brain that is ischemic from that which is infarcted (i.e., irreversibly damaged). Such information would be useful in terms of guiding and monitoring possible therapeutic interventions.

Figure 1 shows an example of a lactate image (and a corresponding T_2-weighted MR image) recorded from a patient with a right internal carotid artery occlusion 24 hours after the onset of his symptoms. Note the elevation of lactate in the right basal ganglia and posterior temporo-parietal lobe; in comparison, the T_2 image is unremarkable, with only slight hyperintensity in the anterior limb of the internal capsule. A follow-up study performed 7 days later shows this region to be clearly infarcted with T_2 hyperintensity and an almost complete depletion of N-Acetyl Aspartate (NAA) (Figure 2).

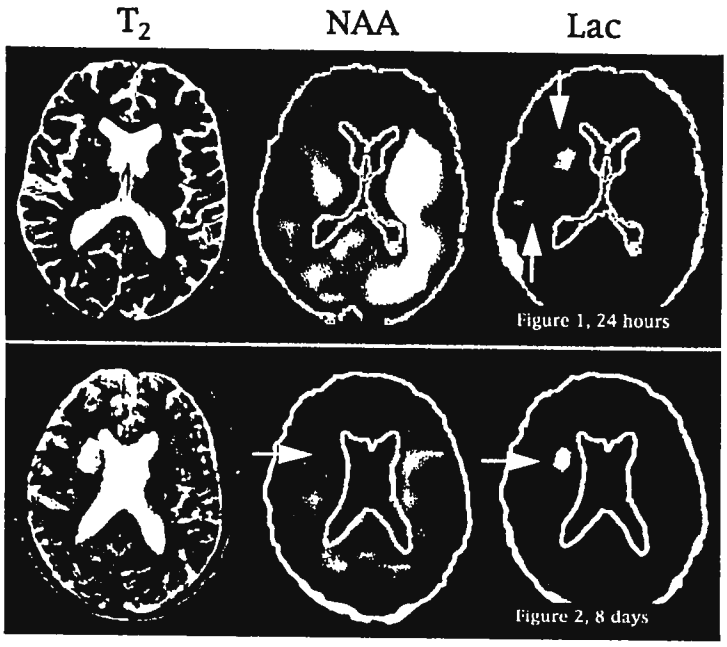
The study nicely illustrates the ability of proton spectroscopy to map ischemic regions in the human brain; it is tempting to speculate that much of the brain was potentially still viable at 24 hours post ictus, based on the preservation of the NAA signal at this time. It is possible that a more aggressive intervention may have resulted in improved patient outcome. This work was performed in collaboration with J.H. Gillard, P.C.M. van Zijl, B.J. Soher, D.F. Hanley, A.M. Agildere, S.M. Oppenheimer, and R.N. Bryan,

Sincerely Yours,

P.B. Barker

Peter B. Barker, D. Phil.,

1. J. Duyn, J. Gillen, G. Sobering, P. van Zijl and C. Moonen, Multislice Proton MR Spectroscopic Imaging of the Brain. *Radiology* **188,** 277-282 (1993).
2. V. Mathews, P. Barker and R. Bryan, Magnetic Resonance Evaluation of Stroke. *Magnetic Resonance Quarterly* **8,** 245-263 (1992).



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All Newsletter correspondence should be addressed to

Dr. B. L. Shapiro
966 Elsinore Court
Palo Alto, CA 94303 U.S.A.

(415) 493-5971 - *Please call only between 8:00 am and 10:00 pm, Pacific Coast time.*

Deadline Dates

No. 428 (May)	22 April 1994
No. 429 (June)	20 May 1994
No. 430 (July)	24 June 1994
No. 431 (August)	22 July 1994

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