

**THE**  
**NMR**  
**NEWSLETTER**

**No. 439**  
**April 1995**

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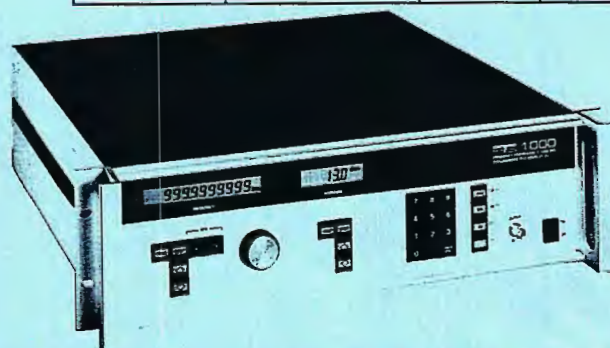
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**FORTHCOMING NMR MEETINGS**

International School of Biological Magnetic Resonance, 2nd Course: Dynamics and the Problem of Recognition in Biological Macromolecules, Erice, Trapani, Sicily, Italy, **May 19 - 30, 1995** (*Note the new dates.*); Contact: Prof. O. Jardetzky, Stanford Magnetic Resonance Laboratory, Stanford University, Stanford, CA 94305-5055; Phone: (415) 723-6270; Fax: (415) 723-2253; or, Prof. J.-L. Lefèvre, ESBS, CNRS-UPR9003, Univ. Louis Pasteur, Blvd. Sébastien Brant, F67400 Illkirch Graffenstaden, France; Phone: (+33) 88-655269; Fax: (+33) 88-655343; See Newsletter 438, 54.

Summer School on "Isotope Effects as Tools in Basic and Environmental Research", Roskilde, Denmark, **June 24 - 28 1995**; Contact: Prof. P. E. Hansen, Fax +45 4675-7721, or Phone +45 4675 7781-2432 or +45 4675-7711, ext. 2432; . See Newsletter 438, 39.

Workshop on "Structure Determination from NMR", Pittsburgh Supercomputing Center, Pittsburgh, PA, **June 25 - 28 1995**; Contact: N. C. Blankenstein: blankens@psc.edu or (412) 268-4960. See Newsletter 438, 29.

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

ISMAR 1995, Sydney, NSW, Australia, **July 16-21, 1995**; Contact: Dr. W. A. Bubb, Dept. of Biochem., Univ. of Sydney, Sydney, NSW 2006, Australia. Phone: +61-2-351-4120; Fax: +61-2-351-4726; Email: ismar95@biochem.su.oz.au. See Newsletter 437, 20.

NMR Symposium at the 37th Rocky Mountain Conference on Analytical Chemistry, Denver Colorado, **July 24-27, 1995**; Contact: Dr. Alexander J. Vega, DuPont Central Research and Development, P.O. Box 80356, Wilmington, DE 19880-0356; Tel. (302) 695-2404; Fax: (302) 695-1664; e-mail: vega@esvax.dnet.dupont.com. See Newsletter 432, 34.

37th ENC (Experimental NMR Conference), Asilomar Conference Center, Pacific Grove, California, **March 17 - 22, 1996**/sicj; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4735; Fax: (505) 989-1073.

38th ENC (Experimental NMR Conference), Orlando, FL, **March 23 - 27, 1997**/sicj; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4735; Fax: (505) 989-1073.

Additional listings of meetings, etc., are invited.

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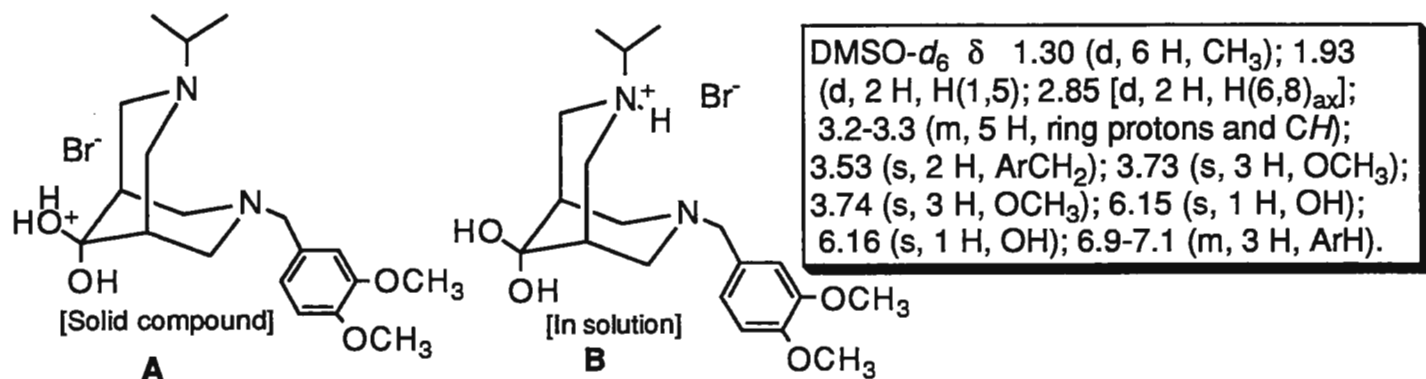
Department of Chemistry  
107 Physical Sciences  
Stillwater, Oklahoma 74078-0447  
405-744-5920  
FAX 405-744-6007

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

March 08, 1995  
(received 3/11/95)

Dear Barry:

Your reminder was timely as always. We have been working on hydrates of 3,7-diheterabicyclo-[3.3.1]nonan-9-ones of late several of which have interesting  $^1\text{H}$  NMR spectra. The system below is novel in that the acidic proton appears to be on oxygen in the solid (Structure A-single crystal X-ray diffraction analysis) while it is on nitrogen (structure B) in solution. This "hydrogen migration" is very rare in this family of heterocycles but not entirely unknown. The shifts for H(6,8) in B are considerably downfield and support



the presence of the protonated nitrogen N-7. Such diols have been reported<sup>1,2</sup> as stable which is presumably due, at least in part, to shielding of the geminal hydroxyl groups by the ring system. We are currently attempting to obtain the NMR spectrum of A in the solid state.

We trust that this will meet our obligation. Best regards.

Sincerely yours,

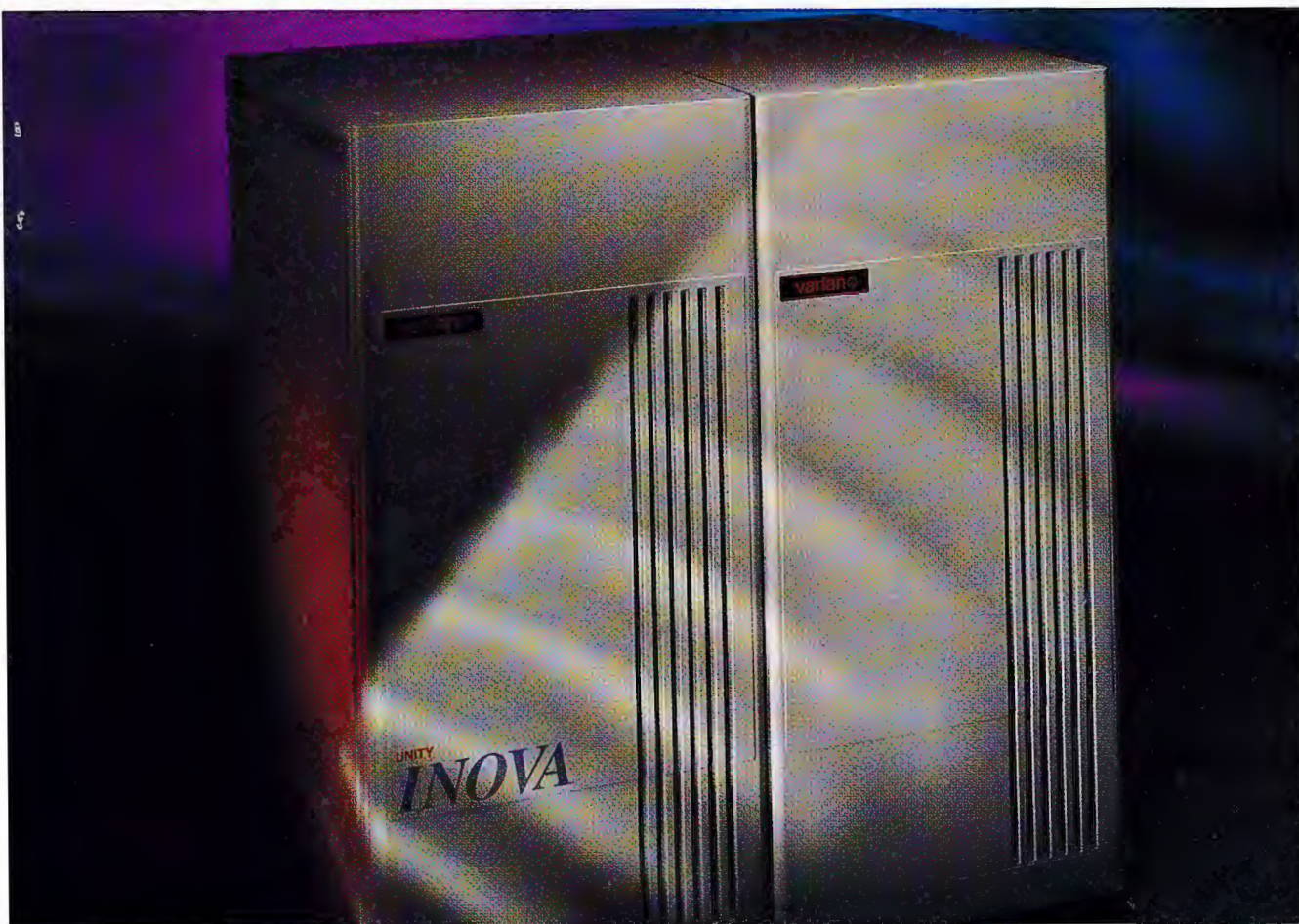
K. Darrell Berlin, Director, NMR Solutions Lab  
Regents Professor

<sup>1</sup>Bailey, III, B. R.; Berlin, K. D.; Holt, E. M. *Phosphorus & Sulfur* **1984**, 20, 131-137.

<sup>2</sup>Smith, G. S.; Thompson, M. D.; Berlin, K. D.; Holt, E. M.; Scherlag, B. J.; Patterson, E.; Lazzara, R. *Eur. J. Med. Chem.* **1990**, 25, 1-8.



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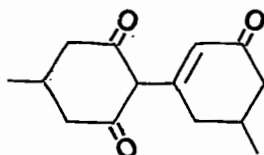
Dr. Bernard Shapiro  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, Ca. 94303

**IS DRY AIR HAZARDOUS FOR A UNITY+500 NMR SPECTROMETER?**

Dear Barry,

A new Varian Unity+500 NMR spectrometer was installed at our facility last year. As with any installation, ours was not without it's problems. The most difficult to solve was a mysterious drop in the lock intensity and a concurrent loss in magnet homogeneity which lasted for approximately 10 seconds and would then go away for a while. It had us stumped until an alert technician noticed that the problem occurred exactly every 5 minutes. Further investigation showed that the source of the problem was a Balston air dryer, which we had to install because of excessive moisture in the house air. The lock intensity would drop approximately 20 seconds after the dryer cycled to the other drying tower. We have had this dryer on our two XL spectrometer for several years and never had a problem. When we installed a surge tank which we were able to purchase from Balston, the problem went away.

We have been quite busy trying to make the transition from an XL-400 to a modern state of the art spectrometer. A problem we have been working on is the identity of an impurity that was recovered from the synthesis of 4-methyl-cyclohexanedione. Only a small amount was recovered so we decided to try a gradient HMQC experiment. A partial spectrum is shown in FIG. 1. It is obvious from the spectrum that there is at least one asymmetric carbon in the molecule as there are at least two sets of chemically different protons which are bound to the same carbon ( $\delta 38$  and  $\delta 45$  ppm). The doublet at  $\delta 2.42$  did not show a correlation to any carbon. From this and other data, the impurity is most likely:



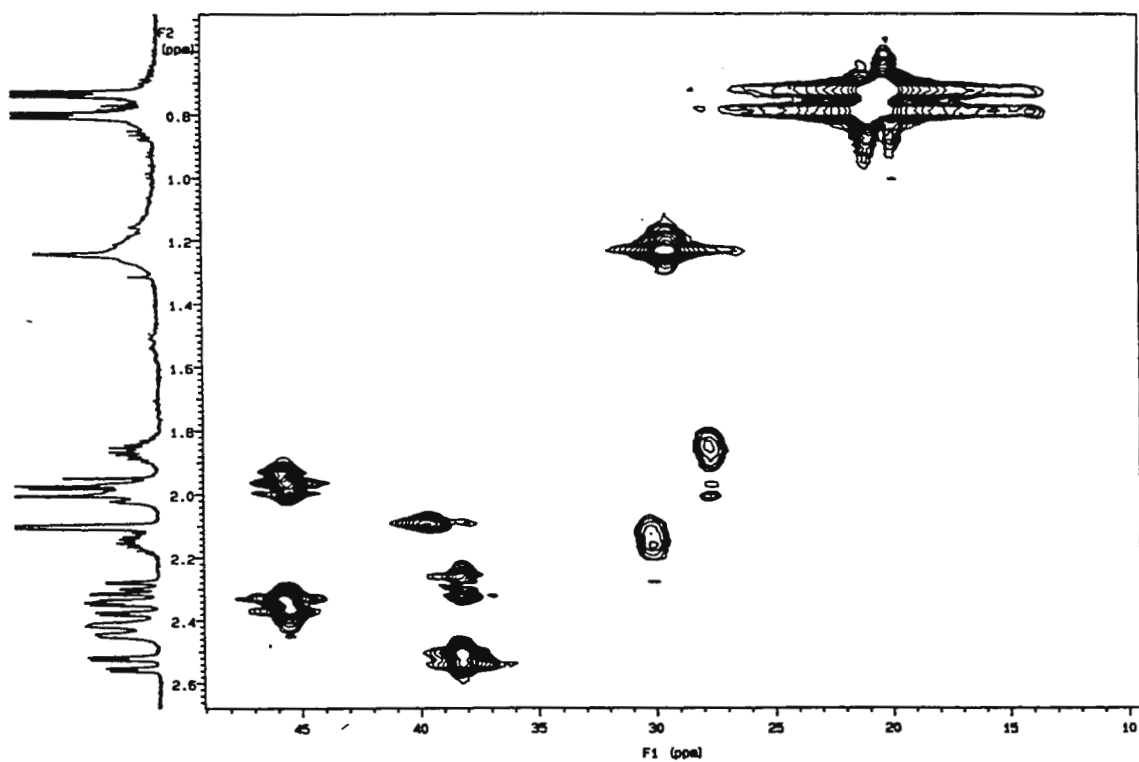
What was most impressive was the ability to get good 2D carbon-hydrogen correlation

data in a reasonable amount of time from a tiny amount of sample (<1 mg). The acquisition of this data on our older spectrometers would not have been possible.

Sincerely yours,

*Lydia Chang*  
Lydia Chang

*Donald Bowler*  
Donald Bowler



A

FIG. 1



Merck Frosst Canada Inc.  
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February 27, 1995  
(received 2/28/95)



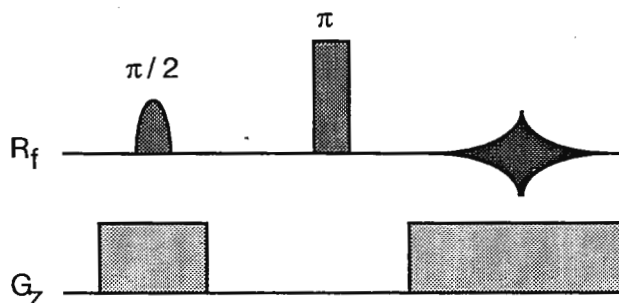
Professor Bernard. L. Shapiro  
966 Elsinore Court  
Palo Alto, CA 94303  
U.S.A.

## Visualizing Shaped Excitation Pulses Using Pulsed Field Gradients

Dear Professor Shapiro,

As I implement more and more selective pulses into various pulse sequences, I find myself repeatedly running into the same problem. The problem is choosing an appropriate pulse length which results in excitation of only those spins that I am interested in and no others. Most spectroscopists, myself included, keep tables of selective pulse length vs. excitation bandwidth for various shapes to avoid repeating these calibrations. However, the explosion of new selective pulses has made keeping such tables for all common pulses difficult.

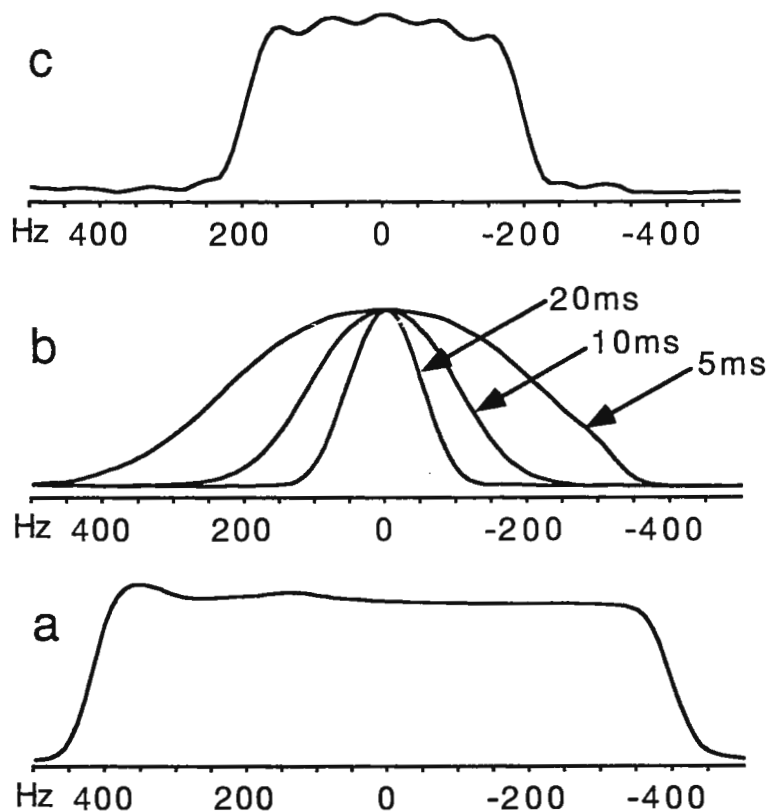
I would like to demonstrate a method that I've implemented on our AMX 500 that helps simplify the construction of the above tables. The pulse sequence, shown below, is stolen directly from the imaging field. To use the vernacular, it is a basic echo imaging sequence with the phase-encoding step removed and the slice selection and read gradients placed on the same axis.



The first gradient spreads the resonance for the water spins over a large frequency range. The selective pulse excites only those spins within its excitation bandwidth. The gradient is then turned off and an echo is generated via the  $\pi$  pulse and the final gradient. Since the final gradient is on during the acquisition period, the water spins are spread out in frequency again and only those spins that experienced the selective  $\pi/2$  pulse are observed. The resulting spectrum is a projection of the excited sample onto an axis perpendicular to that of the gradient.

If the selective pulse is a 6  $\mu$ s high-power square pulse, resulting in uniform excitation across the entire sample, then the spectrum, shown in figure a, consists of a step function because the sample is a cylinder of  $\text{H}_2\text{O}/\text{D}_2\text{O}$ . If a gaussian pulse truncated at the 2% level is used, then the expected gaussian response is observed (figure b). As the length decreases from 20 ms to 5 ms the width at half height increases

from 117 Hz to 479 Hz as expected. When a 25 ms sinc pulse with 5 lobes was used then the expected response of a step function with 5 "bumps" is observed as shown in figure c. These experiments quite readily demonstrate the cost in time of using the sinc function for shaped pulses. For example, a 2% truncated gaussian pulse having a duration of 20 ms has an excitation width of 117 Hz whereas a 25 ms sinc pulse with 5 lobes has a much broader excitation width of 390 Hz.



These spectra were acquired at 500 MHz on a Bruker AMX 500. The sample, a 1mm plug of 1:1 H<sub>2</sub>O/D<sub>2</sub>O in a Shigemii symmetrical NMR microtube, was centered within the gradient coil. Gradients were a modest 1.5 G/cm having durations of 25.6 and 51.2 ms respectively. Spectra were processed with a  $\sin^2$  window and Fourier transformed in magnitude mode.

In figure a, a high power 6  $\mu$ s pulse was used giving uniform excitation across the spectrum. In figure b, three superimposed spectra are shown in which gaussian pulses, having 2% cutoff levels and lengths of 5, 10 and 20 ms, were applied. Spectrum c shows the results obtained with a 25 ms sinc pulse having five lobes.

I think that these results demonstrate how well this method works for determining the excitation profile of selective excitation pulses. With a few modifications, it could be used to observe the bandwidth of selective refocussing pulses also.

Sincerely,

Laird A. Trimble, Ph.D.

# 3-AXIS GRADIENT APPLICATIONS

## MAGIC ANGLE GRADIENT DQF-COSY

The introduction of three axis field gradient spectroscopy in high resolution NMR has led to numerous applications including:

- *Gradient shimming...*  
optimization of magnetic fields by using 3D field image mapping
- *Water exchange filter (WEX)*<sup>1</sup>...  
rapid saturation of water to selectively monitor exchangeable protons
- *and now Magic Angle gradient*

It was recently demonstrated<sup>2,3</sup> that residual water can be refocused in multiple quantum experiments when single axis magnetic field gradients are used for coherence selection thereby causing incomplete water elimination. *This refocusing can be removed by applying coherence selection gradients at the magic angle which is simple using triple axis gradients.*

Using the Bruker GRAdient SPectroscopy III (GRASP III) accessory with x,y,z-gradients, an effective gradient at the magic angle ( $54.74^\circ$ ) can be produced by applying three gradients simultaneously. This greatly improves the elimination of residual water by coherence selection in multiple-quantum-filtered COSY experiments.

This is best illustrated in a comparison of DQF-COSY experiments, one using z-gradient only and the other using magic angle gradient<sup>4</sup>.

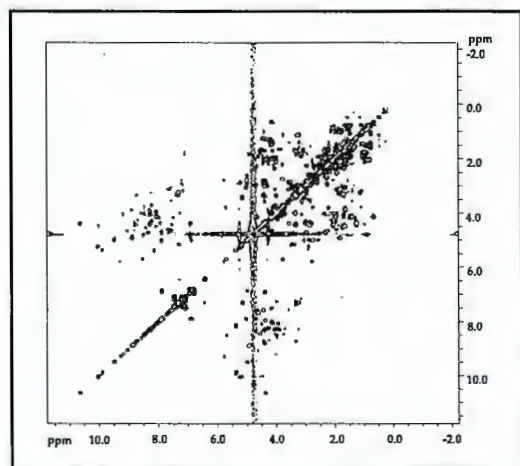


Figure 1: DQF-COSY with z-gradient only

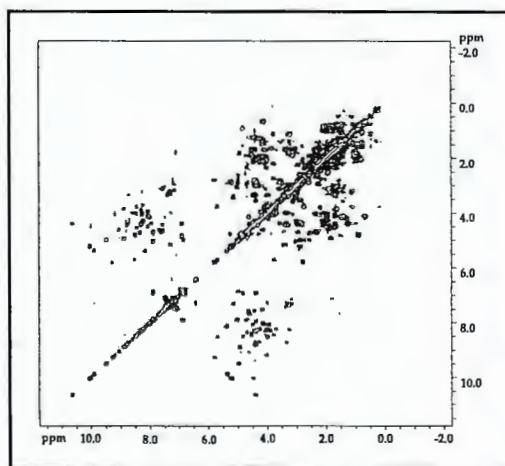


Figure 2: DQF-COSY with magic angle gradient





Both experiments were acquired on a sample of 1.5 mM BPTI in 90% H<sub>2</sub>O/10% D<sub>2</sub>O, using a Bruker *AVANCE*<sup>TM</sup> DMX 500 equipped with a 5 mm inverse triple resonance (TXI) probe with GRASP III. The elimination of the water signal is achieved by coherence selection. **No presaturation is used in either experiment!** The only difference is the application of one gradient versus three gradients.

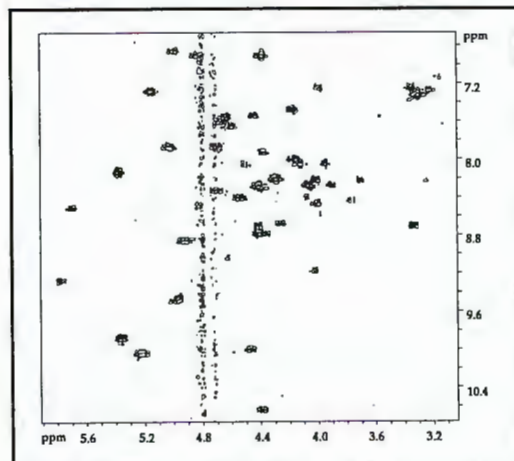


Figure 3: expansion of DQF-COSY with z-gradient only

#### Result with the z-gradient only...

the residual water ridge is clearly visible and overlaps crosspeaks of interest.

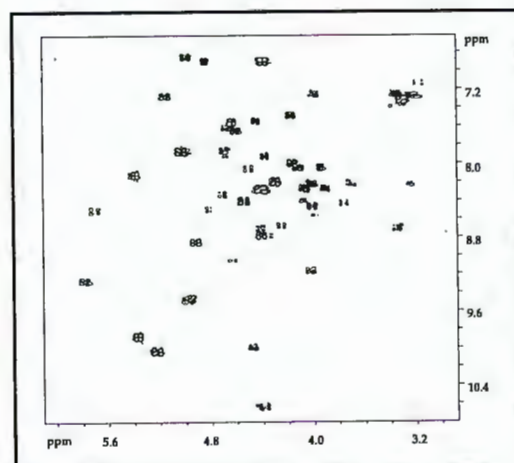


Figure 4: expansion of DQF-COSY with magic angle gradient

#### Result with magic angle gradient...

the residual water ridge is eliminated! Crosspeaks previously overlapped by the water can be observed and used for correlation assignment.

Magic angle gradient provides a simple and effective method for coherence selection in NMR spectroscopy. Just another example of the flourishing three axis gradient applications.

1. S. Mori, M. O'Neil Johnson et al, J. Am. Chem. Soc. **116**, 1994
2. W. Warren, W. Richter, A. Hamilton Andreotti, B. Farmer, Science, **262**, 2005 (1993)
3. R. Bowtell, R. Bowley, P. Glover, J. Magn. Reson, **88**, 643 (1990)
4. P. van Zijl, M. O'Neil Johnson et al, J. Magn. Reson, in press

**Sandia National Laboratories**  
Albuquerque, NM 87185

The NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303

March 23, 1995  
(received 3/24/95)

**Rotor-Synchronized Acquisition for Solid State Isotropic NMR  
Spectra on Bruker ASX Instruments**

The use of rotor-synchronized acquisition of magic angle spinning (MAS) rotational echoes in  $^2\text{H}$  labeled materials to obtain the isotropic ('high resolution') NMR spectra has recently been investigated here at Sandia National Laboratories and the University of New Mexico. One of the major difficulties encountered was development of a functional pulse program allowing the synchronization of the data acquisition with the rotation echoes in the FID. An example of a working pulse program for the Bruker ASX and AMX instruments is given below. Note that even though a simultaneous acquisition mode was employed (aqmod=qsim) two independent external advance calls are required to digitize the complex data points. In addition, there is a software requirement that these calls must be separated by a delay.

; Rotor synchronized single pulse experiment - no decoupler  
; Written Alam: 1/95

```

define loopcounter tdfhalf=td/2

ze
1  d1 tlo dlo do          ; recycle delay
    10u adc               ; enable acquisition
    1u trigp              ; rotor sync - positive
    1u trign              ; rotor sync - negative
    d5                   ; small delay (10 us)
    (p1 ph1):t:e          ; pulse with receiver blanking
    2u:e                 ; hold phase and receiver blanking
    1u ph2:r              ; set phase for acquisition
2  5u                   ; begin data acquisition loop
    1u trigp              ; rotor sync - positive
    1u trign              ; rotor sync - negative
    d6                   ; small delay
    1u:x                 ; sample both channels digitize 1
    1u                   ; delay for A/D
    1u:x                 ; digitize second channel
    1u                   ; delay for A/D
    lo to 2 times tdfhalf ; loop over TD/2 points
    recyc=1   ph3         ; add scan and loop to 1
    wr#0
    exit

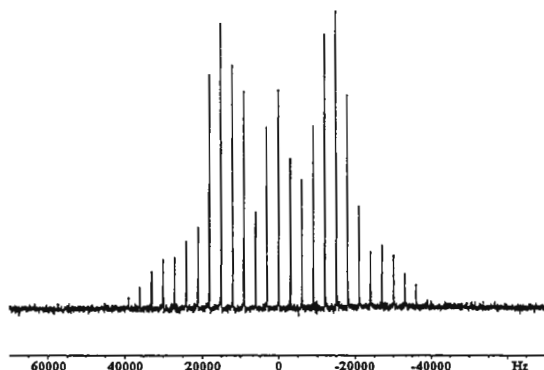
ph1 = 0 1 2 3          ; pulse phase cycle
ph2 = 0                ; reference phase
ph3 = 0 1 2 3          ; receiver phase list

```

The 1 $\mu$ sec delays for and between the external advance calls may need to be longer depending on the type of digitizer utilized. For this pulse program the high speed 12 bit digitizer of the ASX was employed.

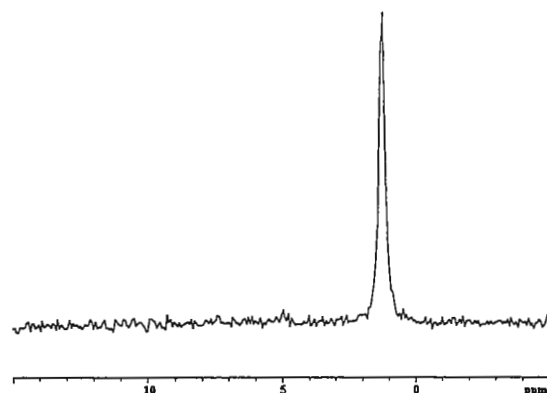
As an example of the improved resolution, MAS  $^2\text{H}$  NMR spectra for [methyl- $^2\text{H}$ ] thymidine with and without rotor synchronized acquisition are shown in Figures 1 A-C. The spectra in Figure 1A reveals rotational sidebands around the center frequency with the envelope approximating the static wide line  $^2\text{H}$  NMR spectra, covering a spectral width of approximately  $\pm 40$  kHz. The rotor synchronized spectra in Figure 1B shows the single isotropic peak expected with a natural line width of approximately 35 Hz. The correct setting of the magic angle is known to have dramatic influence on the observed line shape as evident in Figure 1C, where a misadjustment of approximately  $0.1^\circ$  has produced a broadening and splitting in the observed isotropic spectra.

(A)

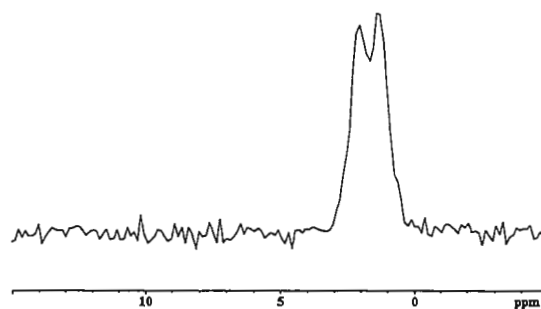


**Figure 1:** (A) Rotational sideband  $^2\text{H}$  NMR MAS spectrum of [ $^2\text{H}$  methyl]-thymidine *without* rotor synchronized sampling, obtained at 46.1 MHz with a rotation speed of 8 kHz. The sideband envelope approximates the non-spinning line shape. (B) Isotropic chemical shift spectrum obtained from rotor synchronized acquisition rotating at 3 kHz. Note change in axis scale. (C) Isotropic spectrum showing effect of 0.1 degree offset in the magic angle.

(B)



(C)



The ability to obtain isotropic spectra from  $^2\text{H}$  NMR solid state experiments in perdeuterated or selectively deuterated materials may prove to be an alternative to  $^1\text{H}$  investigations of these systems. Further investigations are in progress. This work was partially supported by Department of Energy Contract DE-AC04-94A185000.

Sincerely,

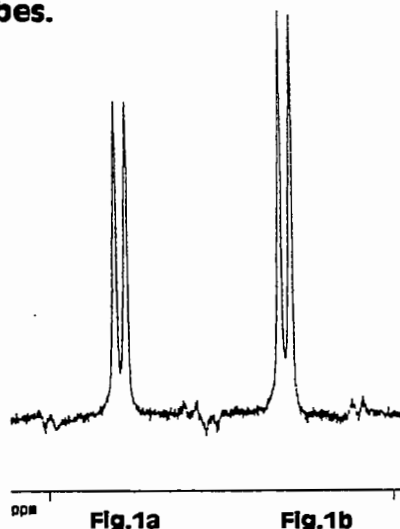
Todd M. Alam

alam@michael.unm.edu

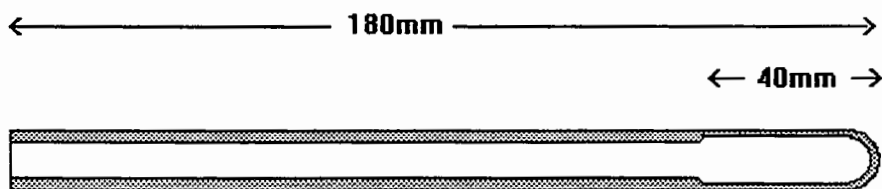


## Specially designed Thin Wall NMR Sample Tube

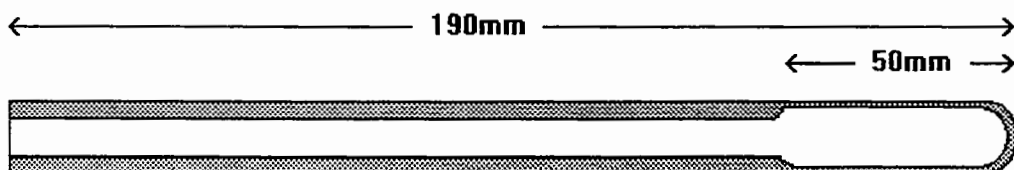
Shigemi's high precision thin wall NMR sample tube has a unique construction. The wall thickness of this particular tube is reduced only around the position of the detection coil. The result of this new invention allows an increase in the sample volume and higher sensitivity without sacrificing its mechanical strength. Therefore, there is no need for special handling during routine usage of our Shigemi NMR tubes.



The spectra of 20mm sucrose in D<sub>2</sub>O 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%.



PST-001 and PST-002



ST8-001, ST8-002, ST10-001, and ST10-002

O.D. (mm)	Product Number	Wall (mm)	Concen- tricity/Camber (μ)	OD (mm)	ID (mm)	Price Each	
						1-99	100 +
5	PST-001	0.21	20/ 8	4.96 + 0.00 - 0.01	4.54 ± 0.01	\$15.00	\$13.50
	PST-002	0.21	40/15	4.96 + 0.00 - 0.01	4.54 ± 0.01	\$13.00	\$12.00
8	ST8-001	0.25	40/ 8	8.00 + 0.00 - 0.01	7.52 ± 0.01	\$31.00	\$28.00
	ST8-002	0.25	50/15	8.00 + 0.00 - 0.01	7.52 ± 0.01	\$27.00	\$25.00
10	ST10-001	0.25	40/ 8	9.98 + 0.00 - 0.01	9.52 ± 0.01	\$36.00	\$32.00
	ST10-002	0.25	50/15	9.98 + 0.00 - 0.01	9.52 ± 0.01	\$32.00	\$28.00

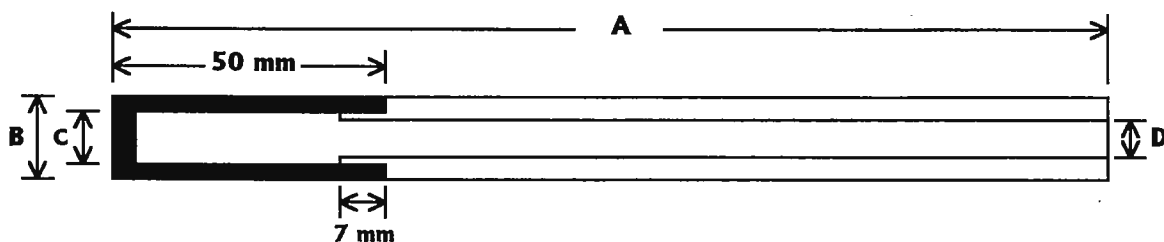
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Type	Diameter	Price for 5 tubes
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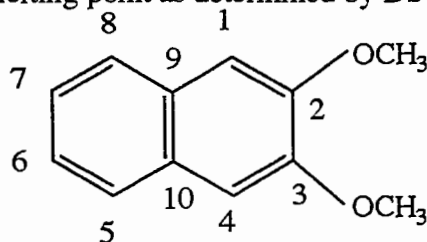


Dr. B.L. Shapiro  
The NMR Newsletter  
966 Elsinore Court  
Palo Alto California, 94303 USA

Feb 4, 1995  
(received 3/15/95)

Title: Intermolecular C-H $\cdots$  $\pi$  Interactions in 2,3-dimethoxynaphthalene As  
Studied By  $^{13}\text{C}$  CPMAS NMR and X-ray Crystallography

Increased  $^{13}\text{C}$  NMR spectral multiplicity in the solid state over solution originates from locked molecular conformations and /or intermolecular packing effects<sup>1</sup>. Recently PhD student Marielle Gerzain has looked at 2,3-dimethoxynaphthalene as part of our program of examining stereoelectronic effects on  $^{13}\text{C}$  chemical shifts in oxygenated organic solids. The structure and numbering scheme of this molecule is shown below. It crystallizes in the P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> space group with 4 equivalent molecules in the unit cell. There are no phase transitions between -60°C and the melting point as determined by DSC.



Based on the bond length, bond angle and torsion angle data, effective C<sub>2v</sub> molecular symmetry exists and hence six  $^{13}\text{C}$  resonances are expected in the solid.

In fact, eight resonances are found, with the largest shift difference being 1.2 ppm between the C5, C8 pair. C1, C4 differ by 0.9 ppm, while the OCH<sub>3</sub> carbons differ by 0.3 ppm.. C9 and C10 differ by only 0.2 ppm and no shift differences are resolved between C2, C3 or C6, C7.

Examination of intermolecular distances reveals a close intermolecular contact (2.67 Å) between C-H<sub>4</sub> of one unit and the C5 site of another. Etter has previously looked at such intermolecular effects<sup>2</sup> and concluded that such interactions should lead to repulsive electronic effects on a site such as C5, hence deshielding it. We have seen similar phenomena in veratrole, but that's another story!

1. M.C. Etter, R.C. Hoyer and G. M. Vojta. Cryst Review Vol 1, 281 (1988).

2. M.C. Etter and G. M. Vojta. J. Mag. Res. 93, 609 (1991).

G.W. Buchanan  
Professor of Chemistry  
Director, Ottawa-Carleton Chemistry Institute

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**TLI** THE LOVELACE INSTITUTES  
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March 9th, 1995  
 (received 3/13/95)

**Automatic ice-maker servicing.**

Dear Dr. Shapiro,

We have a venerable Oxford 1.89T/31cm horizontal bore magnet [model 80/300, project #B26694]. It has been brought down only twice, once in '88 when it needed to be pumped (TAMU Newletter 367-15) and in '90 when it swallowed a peristaltic pump (ibid. 388-47). So, we take its operation very much for granted and are surprised when it decides to call itself to our attention.

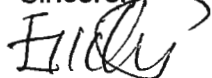
In retrospect, the sound associated with filling the magnet with liquid nitrogen had acquired a "whistling" quality. After this subtle change had been ignored a few months, the whistling became less subtle. Liquid squirting out of the fill port upon disconnecting the inlet hose after a refill prodded us to act.

Everything had the classic signs of a plug in the outlet of the nitrogen chamber. [The big knurled "nut" holding the liquid nitrogen level sensor adjustment circuits was difficult to turn after five years, but we have a very strong visiting scientist (Adolf Feinauer) in the lab.] We found water ice in the exhaust port blocking about 75% of the opening a short way down. Jim Carolan did not think we could chip the ice and blow it out with nitrogen from the other port because things would be too cold but he thought the ice could be knocked into the nitrogen without any harm. Unfortunately, the wire for the nitrogen level sensor was imbedded in the ice which complicated the ice removal.

We connected a 1/4" copper tube to house vacuum (generated by a mechanical pump in the far recess of our building) through Tygon tubing, and warmed the end with a heat gun. Then, the warm end was inserted it into the plug and the Tygon was unpinched to pull some vacuum. When it was retracted, there was a solid plug of ice in the end of the tube. Two repetitions poked a hole through the opening, knocking down the remaining ice onto the connector for the liquid nitrogen sensor. We retrieved most of that ice on the next try. The last bits came flying out when liquid nitrogen was refilled.

So, how did the ice form? Our setup is the simplest possible; flexible tubing venting to atmosphere on both ports. The port that had the problem is the exhaust port during filling and its hose freezes and breaks once in a while. We did not always cut the replacement hoses long enough for their ends to droop below horizontal, thinking that water from the ice that forms on the hose always froze before it got close to the magnet. Evidently we were wrong. Another possibility is that water leaks through the stack from the iceball which forms even in dry New Mexico. A positive pressure setup would prevent this problem but we like the simplicity of venting to atmospheric pressure. If the problem recurs in five years, we will reconsider this view and write another note to this publication.

Sincerely,



Eiichi Fukushima

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## Benefits

<b>Full Multinuclear Range:</b> .....	The X ( <sup>75</sup> As- <sup>31</sup> P) and Y ( <sup>25</sup> Mg- <sup>81</sup> Br) channels provide a complete range of nuclei combinations for the most demanding of experiments.
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<b>PENCIL™ Rotor Design:</b> .....	Large sample volume results in decreased experiment time and increased sensitivity.
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<b>Exclusive VT Stack Design:</b> .....	Permits full temperature range to be exploited without compromise of the probe performance.

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Spinning Speed (ZrO <sub>2</sub> rotors)	1-12 kHz
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"X" Channel Frequency Range	<sup>75</sup> As- <sup>31</sup> P
"H" Channel Frequency Range	<sup>19</sup> F- <sup>1</sup> H
Temperature Range	-150°C to +250°C
Sample Volume	160 µL
<sup>1</sup> H 90° Pulse Width	≤3.0 µs
<sup>13</sup> C 90° Pulse Width (X)	≤4.0 µs
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March 16, 1995

(received 3/24/95)

Dr. Bernard Shapiro  
The NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303

#### Kinetics of Chemical Dehydration of Coals using $^1\text{H}$ NMR

Dear Barry:

In my last letter to you (TAMUNMR 431) I described a  $^1\text{H}$  NMR method to measure the water content in coals using 2,2-dimethoxypropane (DMP) as the dehydration agent. The program has been extended to determine the kinetics of the dehydration of coals using the NMR method described to measure the moisture content as a function of time.

A plot of the weight percent of moisture removed from the Eagle Butte subbituminous coal as a function of time in which the coal was in contact with DMP is shown in Figure 1. Other coals give similar plots. In all cases a significant amount of moisture is removed in the first minute of the reaction. The initial reaction is DMP with physisorbed surface water and free water in the pores near the surface of the coal. Removal of the remaining moisture requires longer times and is due to diffusion control of DMP into the smaller pores within the coals.

The chemical drying data after the fast initial reaction were fitted to 1st- and nth-order kinetic equations. The initial concentration expressed in the equations (not given) is defined as the percent of physisorbed and free surface moisture removed from the coal during the initial reaction of water and DMP. This reaction occurs almost instantaneously.

Based on a first-order kinetics analysis of the dehydration data for several coals, the Utah Blind Canyon coal has the lowest amount of surface water (12.2%) whereas the Texas Bottom coal and North Dakota Beulah lignite have almost two-thirds of the total water near or on the surface and readily accessible to react with DMP (62.0 and 64.4%, respectively). Figure 2 is a plot of the percent of surface water as a function of the rank of coal based upon the fixed carbon content. Wroblewski and Verkade (Energy and Fuels, 1992, 6, 331) also measured the different types of moisture in coals using several extraction solvents and measuring the moisture content in the extracts over an eight hour period. These authors found that of the total moisture content in higher rank coals have less surface water than the lower rank coals in qualitative agreement with the results shown in Figure 2.

The  $^1\text{H}$  NMR-chemical dehydration method provides a technique to obtain the relative percentages of external surface and internal pore water in coals which cannot be obtained by any other method. The amount of external (surface) and internal (pore and hydrogen bonded) water in coal is important and essential to the study of the role of water in coal liquefaction.

Sincerely,

A handwritten signature in cursive script, appearing to read 'Dan'.

Daniel A. Netzel

A handwritten signature in cursive script, appearing to read 'Francis'.

Francis P. Miknis

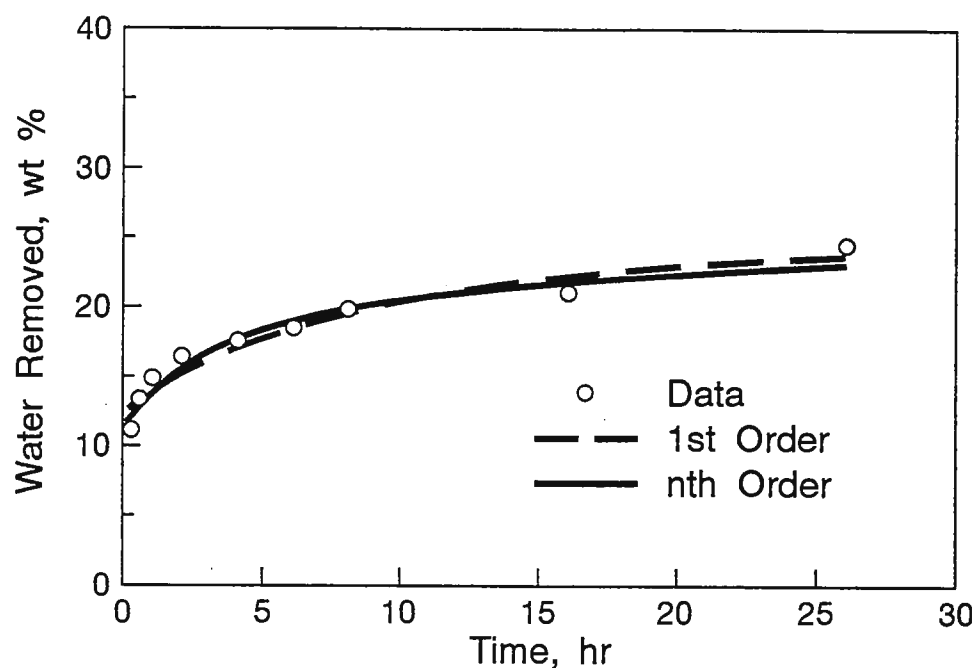


Figure 1. Weight Percent of Water Removed by DMP and Measured by  $^1\text{H}$  NMR in Eagle Butte Coal as a Function of Time

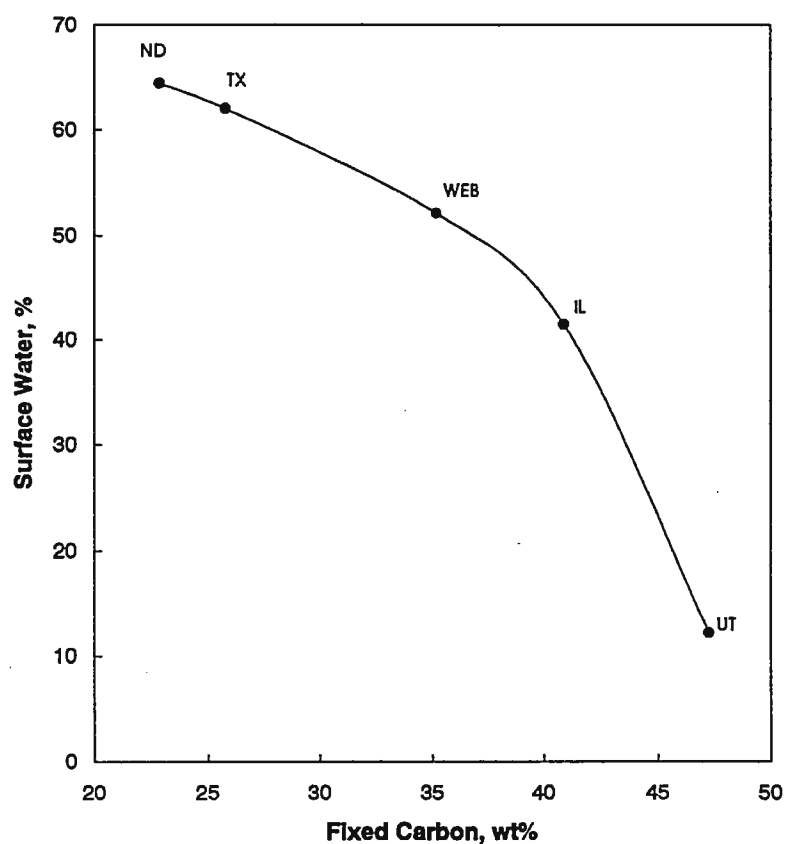


Figure 2. A Plot of the Percent Surface Water for Coals as a Function of the Coal Rank (wt % of fix carbon)

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Pulse width	20 ms	20 ms
Duty cycle	Up to 10%	Up to 10%
Amplitude droop	5% to 20 ms typ.	5% to 20 ms typ.
Harmonics	Second: -25 dBc max. Third: -24 dBc max.	
Phase change/output power	10° to rated power, typ.	
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## Department of Biochemistry

104 Willard Hall  
Manhattan, Kansas 66506-3702  
913-532-6121  
FAX: 913-532-7278

March 7, 1995  
(received 3/13/95)

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

Dear Dr. Shapiro:

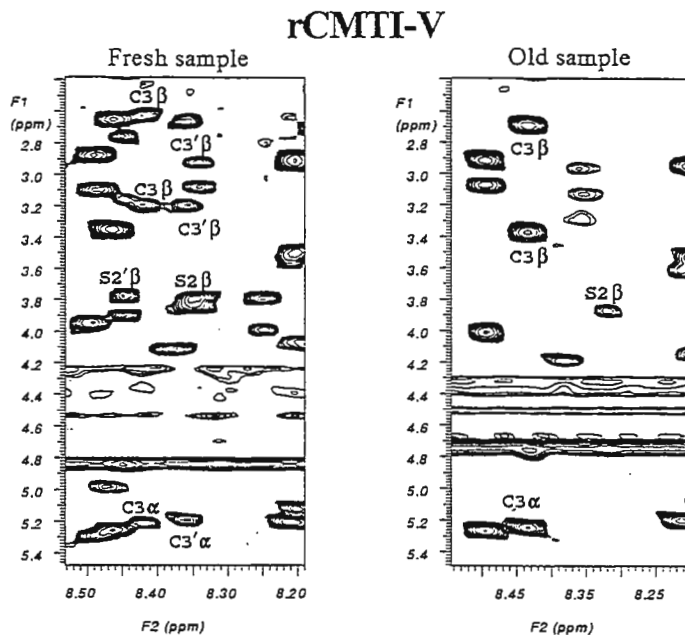
### Conformational Heterogeneity in Recombinant *Cucurbita maxima* Trypsin Inhibitor-V (rCMTI-V)

We recently completed the three-dimensional solution structure determination of native CMTI-V, which is also a specific inhibitor of human blood coagulation factor XII<sub>a</sub>. CMTI-V, isolated and characterized for the first time in our laboratory, has 68 amino acid residues, including a Cys3-Cys48 disulfide bridge, and belongs to the Potato I inhibitor family. In a continuing effort to delineate structure-function relationships in this protein inhibitor, we have been working with recombinant and mutant forms of CMTI-V for the past few months. These proteins were produced by our collaborator, Dr. Lisa Wen, and her research group at the Western Illinois University, Macomb, Illinois. These proteins differ from the native material in that they each contain a sequence of 7 additional residues at the N-terminus (numbered -7 to -1). Furthermore, the native protein is N-acetylated, whereas the recombinant proteins are not.

In the course of purification of the genetically engineered proteins by reverse-phase high performance liquid chromatography, we observed two protein peaks, instead of one, and one of them grew at the expense of the other, over a period of weeks, yielding a single peak. This type of heterogeneity is not observed in the native protein.

Detailed NMR studies, employing both 2D and 3D techniques, have revealed the presence of two sets of cross peaks for some residues in a freshly prepared rCMTI-V sample, of which one set disappears in the course of time. The figure shown below identifies two sets of TOCSY cross peaks for Ser2 and Cys3; one of them disappears after about 10 days.

We are currently attempting to identify the source of heterogeneity. A proline residue occurs at position 4 in the sequence, and because of the well-known proline *cis-trans* isomerism, that residue is currently our lead suspect. Lisa is in the process of preparing a P4G mutant for us to confirm or eliminate our suspicion.



Sincerely,

*Mengli Cai*

Mengli Cai

*Jianhua Liu*

Jianhua Liu

*Ying Huang*

Ying Huang

*YuXi Gong*

YuXi Gong

*Om Prakash*

Om Prakash

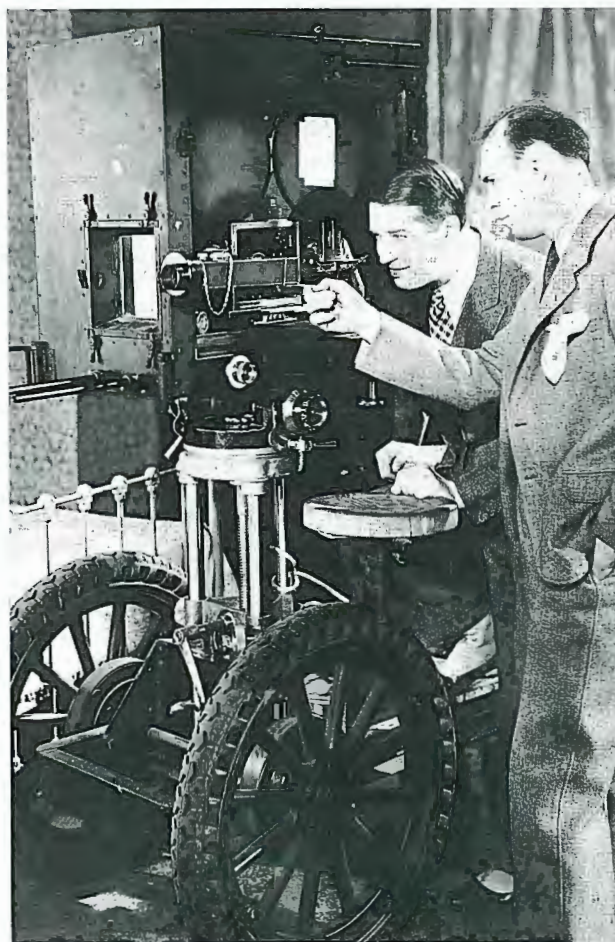
*R. Krishnamoorthi*

R. Krishnamoorthi

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600	51	10	120	3.4
500	51	10	150	3.2
400	54	8	365	2.8
360	54	8	365	2.8
300	54	3	365	2.8
270	54	2.7	365	2.8
200	54	2	365	2.8
100	54	1	365	2.8
500	89	15	120	3.4
400	89	10	180	2.8
360	89	10	365	2.8
300	89	3	365	2.8
270	89	2.7	365	2.8
200	89	2	365	2.8
100	110	1	119	2.8

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March 6, 1995

B.L. Shapiro, Publisher  
The NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303

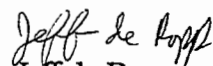
**RE: Omega Orphans Internet Group**

Dear Dr. Shapiro:

We have formed an Internet group for those former GE-NMR customers with Omega instrumentation, the informally titled and very loosely associated "Omega Orphans". This is patterned after the well-known and superb AMMRL and BUM/Varian email groups. We are not a subgroup of those excellent groups since they are growing in membership and scope while this group will have a finite number of potential members and will eventually go out of business. Nonetheless, for those interested in exchanging useful information on Omega software, hardware, and applications the group can be joined by emailing a subscribe request to [strain@mango.uoregon.edu](mailto:strain@mango.uoregon.edu). Regular email traffic for the Omega-Net should be sent to [omega-net@mango.uoregon.edu](mailto:omega-net@mango.uoregon.edu). We hope that this exchange of information will prolong and expand the utility of our Omega instrumentation. We welcome all Omega users to join this group.

Sincerely,

Mike Strain  
University of Oregon  
[strain@mango.uoregon.edu](mailto:strain@mango.uoregon.edu)

  
Jeff de Ropp  
UC Davis  
[jsderopp@ucdavis.edu](mailto:jsderopp@ucdavis.edu)



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10 March 1995 (received 3/20/95)

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

Dear Dr. Shapiro,

About 18 months ago, we installed gradients capabilities (2) on our 600 MHz spectrometer. Due to various problems with the probehead (e.g. several breakages of the gradient coil), we were rather slow in implementing gradient-enhancements in many of our triple resonance experiments. When we finally got round to doing so, more surprises and frustration awaited us.

It is accepted that introducing gradient pulses in many experiments will result in at least a factor of  $\sqrt{2}$  loss in signal to noise (ratio S/N). Hence one can naively obtain two spectra, with and without gradients, compare the S/N approximately and then presumably accept that everything is functioning properly if the decrease in S/N due to the introduction of the gradient pulses is approximately  $\sqrt{2}$ .

We discovered that a more stringent test is to perform a sensitivity-enhanced gradient-enhanced (GE) experiment. In this case the full S/N should be recovered, that is, there should be no difference in the S/N between a GE and a non-GE experiment.

We find that this latter method is a very reliable method of checking the performance of the gradient system. As a result, we have been able to efficiently highlight malfunctions in one or several components of the gradient system (amplifier, preemphasis and probehead).

We hope that your readers have more success with their gradient system than we had!

Please credit this contribution to G.C.K.Roberts.

Yours sincerely,

Lu-Yun Lian

Igor Barsukov



# TEXAS A&M UNIVERSITY

Department of Chemistry  
College Station, Texas 77843-3255  
(409) 845-2011  
FAX (409) 845-4719  
March 6, 1995

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

## <sup>13</sup>C as a relaxation mechanism in Proton spectroscopy

(received 3/13/95)

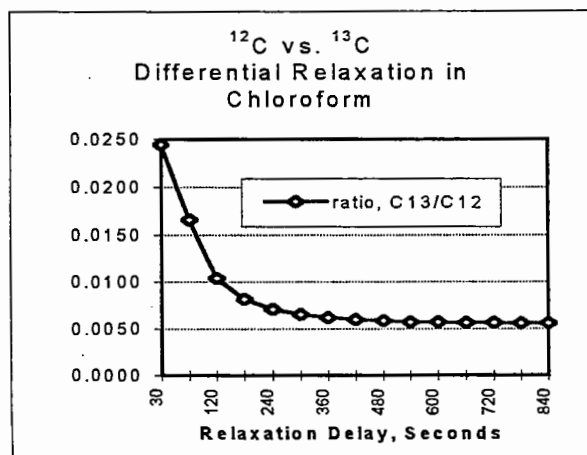
Dear Barry:

We all know that a dipolar interaction with a directly bound proton is generally the single most efficient mechanism for relaxing a carbon nucleus, but it is seldom that we think about this the other way around - that a directly bound carbon atom may be the most efficient mechanism for relaxing a proton. This is the case for chloroform, however. Chloroform is now routinely used to specify proton lineshape performance, and the intensity of the <sup>13</sup>C satellite is normally used to determine the 0.55% and 0.11% intensity levels. It has been known in at least some circles, but perhaps not widely, that the <sup>13</sup>C satellite lines relax more quickly than the central <sup>12</sup>C bound proton resonance due to the dipolar interaction.

Dr. Hong Jun Pan, who has been doing solid state NMR for the Chemistry Department for several years, recently joined me in doing solution state NMR as well. As part of his introduction to solution state work and the Varian spectrometers, he measured the proton relaxation times of chloroform, comparing the relaxation rates for the <sup>12</sup>C and <sup>13</sup>C bound protons. We measured 21.1 seconds,  $\pm 0.9$  seconds for the downfield <sup>13</sup>C satellite signal, and 158.3 seconds  $\pm 1.4$  seconds, for the central <sup>12</sup>C resonance, a factor of 8 in relative relaxation times.

I took these relaxation times and generated a spreadsheet calculation showing the intensity of the <sup>13</sup>C satellite relative to the central line as a function of the relaxation delay. You can readily see that a relaxation delay on the order of 500 seconds is required to insure accurate determination of the 0.55% intensity level and that a delay of only 1 minute results in a 3-fold increase in the apparent intensity of the <sup>13</sup>C satellite signal. Signal intensities were calculated simply as  $I_{c12} = 98.9 * (1 - e^{-t/158})$  and  $I_{c13} = 0.55 * (1 - e^{-t/21})$ . The ratio of these two values is then the relative intensity of the <sup>13</sup>C satellite.

Delay	Intensity, C12	Intensity, C13	ratio, C13/C12
30	17.09	0.4182	0.0245
60	31.22	0.5184	0.0166
120	52.57	0.5482	0.0104
180	67.18	0.5499	0.0082
240	77.17	0.5500	0.0071
300	84.00	0.5500	0.0065
360	88.68	0.5500	0.0062
420	91.88	0.5500	0.0060
480	94.06	0.5500	0.0058
540	95.56	0.5500	0.0058
600	96.58	0.5500	0.0057
660	97.28	0.5500	0.0057
720	97.76	0.5500	0.0056
780	98.09	0.5500	0.0056
840	98.31	0.5500	0.0056



The lesson here is to beware of the long  $^{12}\text{C}$  relaxation time in chloroform lest the line shape numbers you measure be artificially low. I wonder how many system installation engineers rigorously wait 10 minutes between pulses when measuring lineshape performance during probe installations, especially since a faster rep rate not only saves time but also gives slightly better lineshape values. This will not be tremendously critical for periodic comparisons of probe performance, assuming that the same delay is used each time, but it is more important when trying to compare numbers with another lab or a spec sheet.

I might also mention that we have all of our spectrometers networked now, and we are starting to get PC-based X-servers around the department so that users can do more of their data processing off-line from the spectrometers. In this particular case, the relaxation experiment was run on our old (1976!) XL-200 system and the data sent by LimNet to a Sparc10 workstation running VnmrX. I then used my office PC as an X-server to process, analyze, and plot the data. I resisted the temptation to use all of the cute Windows tools that would permit cutting and pasting spectra and relaxation curves into this note, although all of these things now work very seamlessly together.

Sincerely,



Hong Jun Pan  
Research Instrumentation  
Specialist



Steven K. Silber  
Senior Research  
Instrumentation Specialist

To commemorate  
The 100th anniversary of Roentgen's discovery and  
The 50th anniversary of Magnetic Resonance  
**The University of Texas Southwestern Medical Center at Dallas**  
will hold a half-day symposium entitled

**New Directions in Biomedical MR Imaging and Spectroscopy**

Wednesday, May 17, 1995

The symposium will include a reception and a buffet dinner. The evening speaker will be Prof. Axel Haase who will discuss aspects of the history of imaging and the future of high speed MRI.

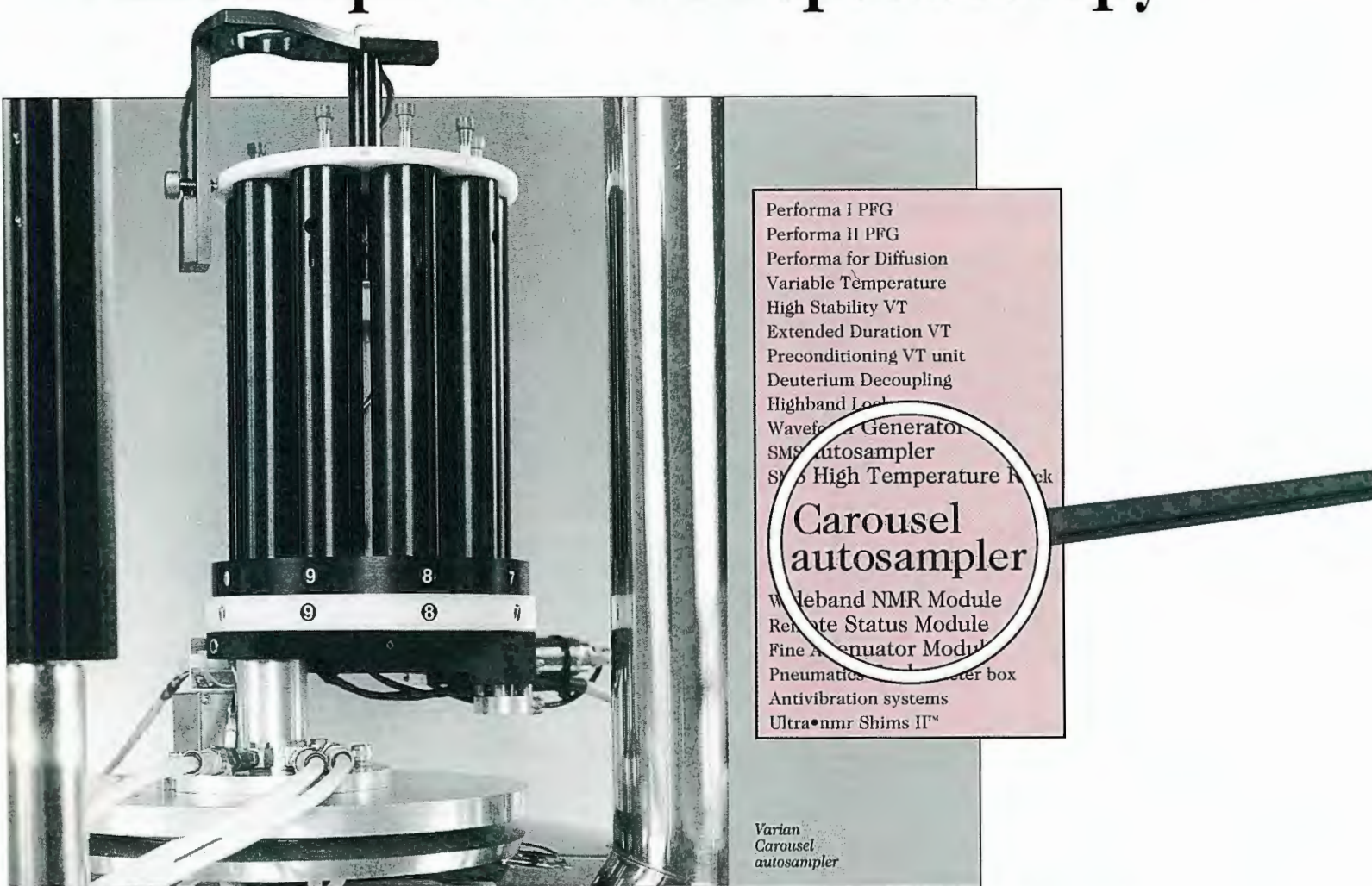
**GUEST SPEAKERS:** Axel Haase, (U of Wurzburg), Paul Matthews, (Montreal Neurological Institute), Peter van Zijl (Johns Hopkins).

**UT SOUTHWESTERN SPEAKERS:** Navin Bansal, Loren Bertocci, James Fleckenstein, Craig R. Malloy, Ronald Peshock, A. Dean Sherry.

**For more information call:** Dr. Navin Bansal (214) 648-5886, Fax: (214) 648-5881.



# Varian Introduces New Carousel Autosampler for NMR Spectroscopy



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The new Carousel autosampler from Varian provides a low-cost, reliable automation solution for a wide variety of NMR laboratory settings. The result of yet another joint development project with Zymark Corporation, the recognized leader in laboratory automation, the Carousel increases productivity with the latest state-of-the-art components.

Capable of running up to nine high resolution samples unattended, the Carousel allows completely random access to all sample locations, providing a more flexible automation system relative to competitive products. Sequential operation is not required and the priority of samples can be changed easily.

The air-actuated drive mechanism of the Carousel is compatible with even the highest magnetic field strengths, and an optical sensor verifies the sample location. The turret of the Carousel is easily removed for adding or removing samples away from the magnet. Alternatively, samples can be added or removed from the Carousel while in place on the magnet.

The Carousel autosampler is compatible with all automated NMR consoles from Varian, including XL, VXR, Gemini, *GEMINI 2000*™, UNITY, *UNITYplus*™, and *UNITYINOVA*™. Please contact your local Varian sales representative for ordering information.

***The first name in nmr...***



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### Highest Throughput

Maximize productivity with the SMS (Sample Management System) autosampler and Varian's *GEMINI 2000™*, *UNITYINOVA™*, and earlier-model automated NMR spectrometers. Fully automatic data acquisition and processing software allows for unattended operation and provides the most efficient use of resources. Fast delivery/retrieval to and from the magnet ensures that sample turnaround is optimized.

### Unmatched Reliability

State-of-the-art robotics minimizes the risk to equipment and samples while maintaining dependable automated operation. The self-calibrating system ensures reproducible positional accuracy while a tactile sensing capability provides verification of robot functions. Use of Varian's Auto•nmr™ probes with the SMS autosampler provides the most reliable automated NMR capability available.

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Data acquisition and robot control are provided by the same computer, allowing users to focus on results, not additional software. Switching between walk-up and automation modes simply requires a single command, and sample submission is possible at any time due to easily accessible sample racks.

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30-second full cycle sample change time.....  
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 Integrated with NMR software.....  
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# DEPARTMENT OF CHEMICAL PHYSICS

e-mail: ciluz@weizmann.weizmann.ac.il

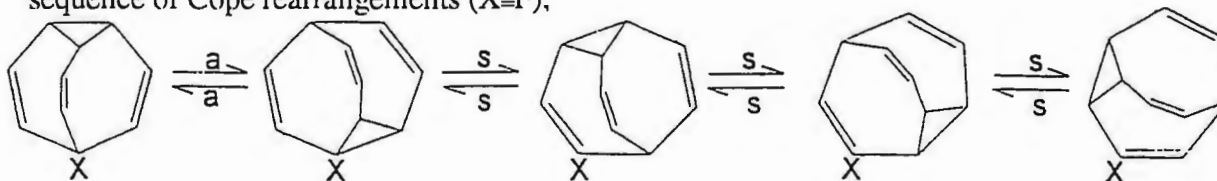
March 15, 1995  
(received 3/23/95)

B.L. Shapiro, Publisher  
The NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303.

Dear Barry,

re: Auto cross peaks and hetero cross peaks

In two-dimensional exchange experiment under conditions of magic angle spinning (with rotor synchronized mixing times) two types of cross peaks may appear; those linking side bands of the same atomic sites in the crystal (auto cross peaks) and those linking side bands of different atomic sites (hetero cross peaks). In the absence of spin diffusion, the appearance of hetero cross peaks report on exchange between different sites, while the auto cross peaks indicate molecular reorientation. Although these rules are well known they seldom need to be applied in the same system. The two carbon-13 2D exchange spectra of solid fluorobullvalene shown in the figure provide an example for one of these rare cases. Both spectra were recorded at room temperature but at widely different mixing times, 20ms and 20s respectively (the carbon  $T_1$ 's are about 10 min). It may be seen that at  $\tau_m=20$ ms there are intense auto cross peaks for carbons 2 and 3, but no hetero cross peaks and no auto cross peaks for carbon 4. This indicates that the molecules reorient about their  $C_3$  axis. At  $\tau_m=20$ s strong hetero cross peaks linking the signals of carbons 1,2 and 3 (but not 4) are also observed, indicating the occurrence (on a much longer time scale) of a dynamic process that permutes all atoms in the molecule except the fluorine bound carbon. A detailed analysis of these cross peaks as function of  $\tau_m$  shows that they are consistent with the following sequence of Cope rearrangements ( $X=F$ ),



*R. Poupko*

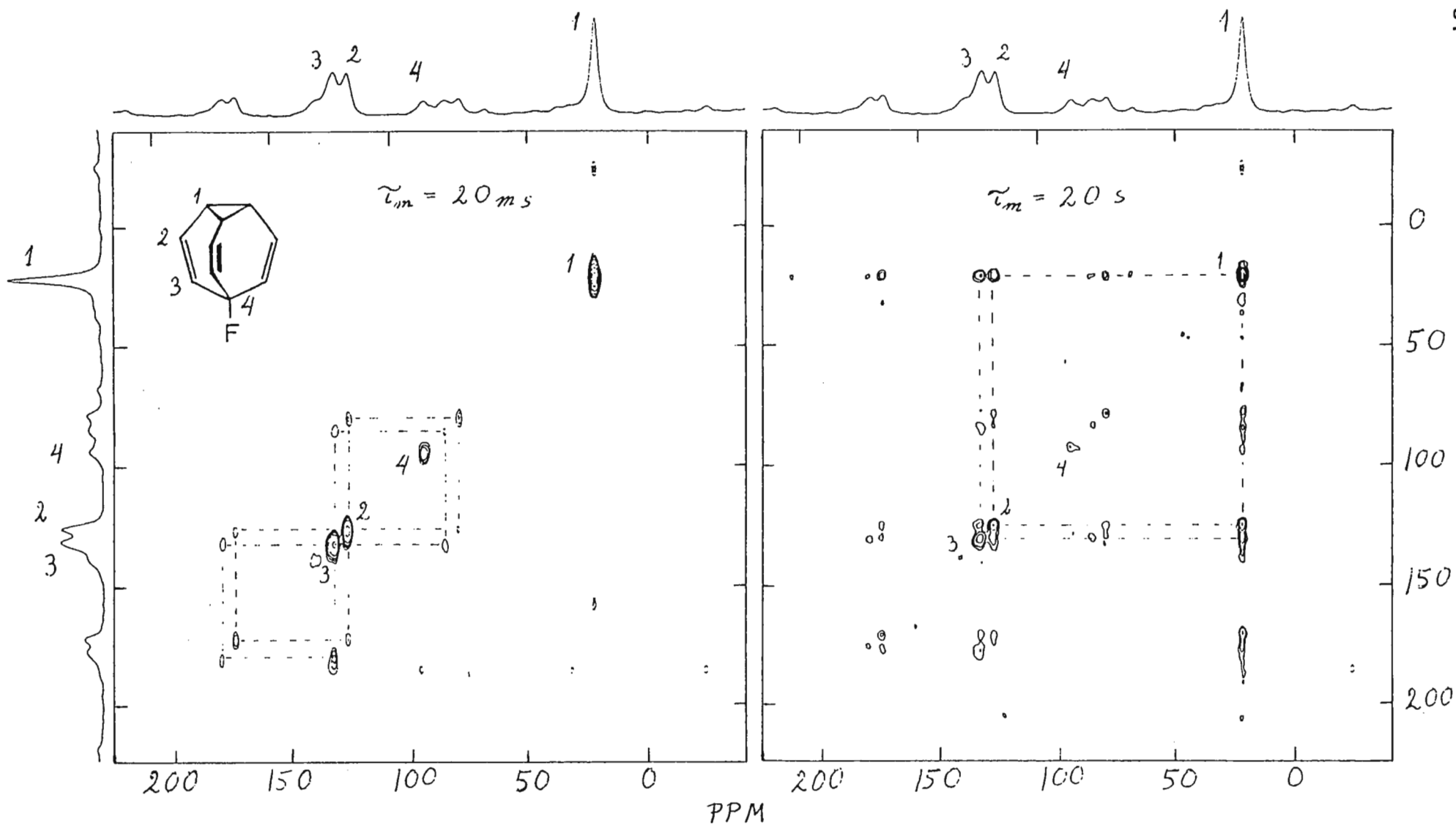
R. Poupko

K. Müller

H. Zimmermann

*Z. Luz*

Z. Luz



Room temperature carbon-13 rotor synchronized MAS 2D-exchange spectra ( $\nu_R=3.5\text{kHz}$ ) of fluorobullvalene. One dimensional MAS spectra and peak assignment are also shown. The dashed curves link cross peaks to the corresponding diagonal peaks and serve to guide the eyes.



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



(received 3/4/95)

Dear Dr. Shapiro:

We would like to announce the availability of a new computer program that we believe will be of wide interest to NMR spectroscopists. **NMRView** is a comprehensive program for the visualization and analysis of processed NMR spectra. The program includes molecular structure analysis and visualization features so that spectral analysis and structure generation can be a tightly linked process. One of the most useful features of **NMRView** is the incorporation of the command language, **Tcl**. This allows users to extensively customize and automate the program. The program itself is described in detail in the *Journal of Biomolecular NMR* (1994, 4:603-614). Here we summarize some of the features of **NMRView** and describe our plans for its distribution:

#### **NMRView Features**

- Multiple views of one or more NMR spectra.
- Unlimited number of spectral windows.
- Windows may be in any size or position on the screen.
- Unlimited number of data files.
- Generic reader for block structured files.
- Corresponding cursors in different windows track each other automatically.
- Contour plots of any plane of any 2,3 or 4 dimensional spectra.
- 1D vector plots in any orientation of 1 to 4 dimensional spectra.
- Spectral displays may be transferred from one window to another using a Copy/Paste protocol.
- Automatic peak-picking.
- Peak searching.
- Facilitated peak analysis and interactive peak editing.
- Spin-system tabulation.
- XY data plotting and non-linear regression analysis.
- Powerful command language (Tcl, tool command language).
- Programmable user interface.
- Flexible Database.
- Comprehensive NOE constraint generation and analysis.
- Structure analysis including rmsd superpositions and constraint violation analysis.
- Molecular Graphics Display with the linked program MDV.
- Contextual Help.
- On-line hyper-text documentation using Web browsers such as Mosaic.

We are making **NMRView** freely available to the NMR Community. At present **NMRView** runs on IBM RS/6000, Silicon Graphics, and SUN workstations. At present we do not plan to release source code, but **NMRView** can be extended extensively through the **TCL** command language. We encourage **NMRView** users who generate useful **TCL** scripts to send them to us and we will distribute them to all who are interested. Furthermore, users with stand-alone modules for various types of NMR analysis are encouraged to contact us.

Where the code appears compatible in spirit and practice with the design and implementation of NMRView, is of broad interest and our time allows we will gladly try to integrate the code into NMRView. We are also interested in collaborative projects to extend NMRView to new methods of analysis. We also welcome suggestions for improvements and notification of bugs. We intend to distribute NMRView only by means of electronic file transfers. We request that all users obtain a copy directly from us and do not distribute the program outside of their own site. Users should reference the J. Biomol. NMR article in manuscripts describing research that used NMRView.

We have set up a NETLIB mail server for distribution of NMRView. Users can send a mail message to:

**netlib@merck.com**

The body of the message should contain the line:

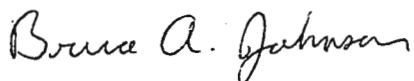
**send about.nmrview from NMRView**

A mail message will be returned containing information about obtaining the NMRView program.

Other inquiries concerning NMRView should be sent to:

**bruce\_johnson@merck.com**

Bruce A. Johnson



Department of Molecular Design and Diversity

Richard A. Blevins



Department of Bioinformatics

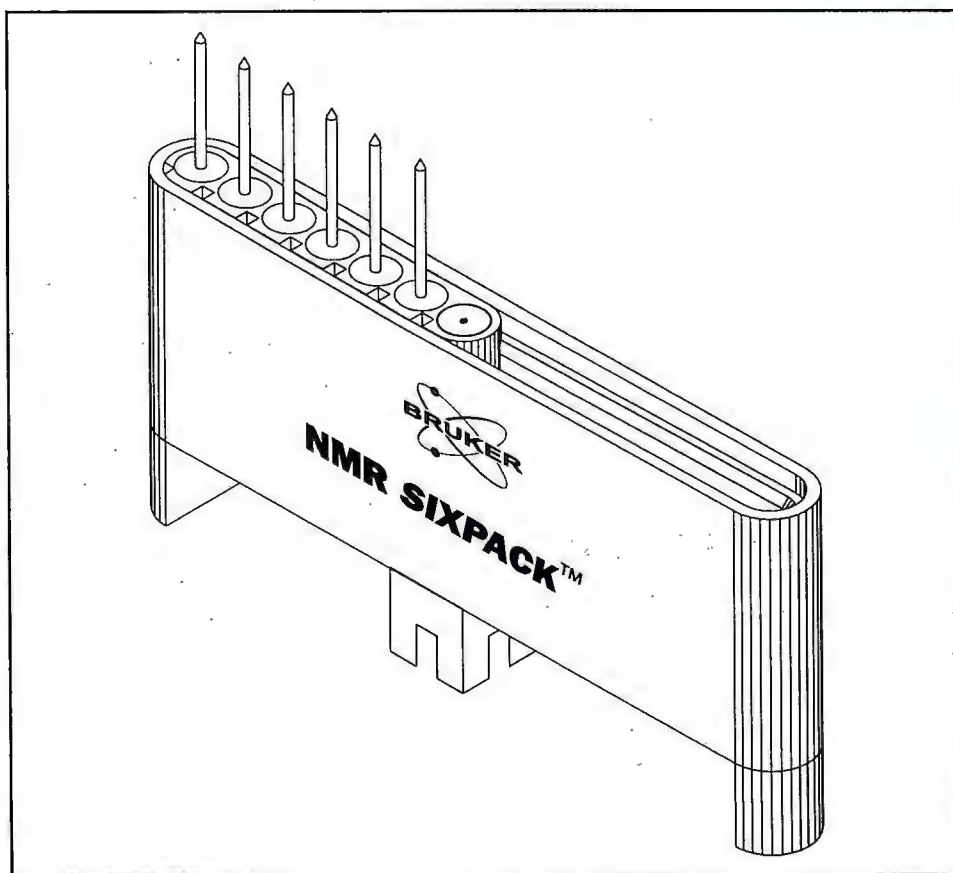
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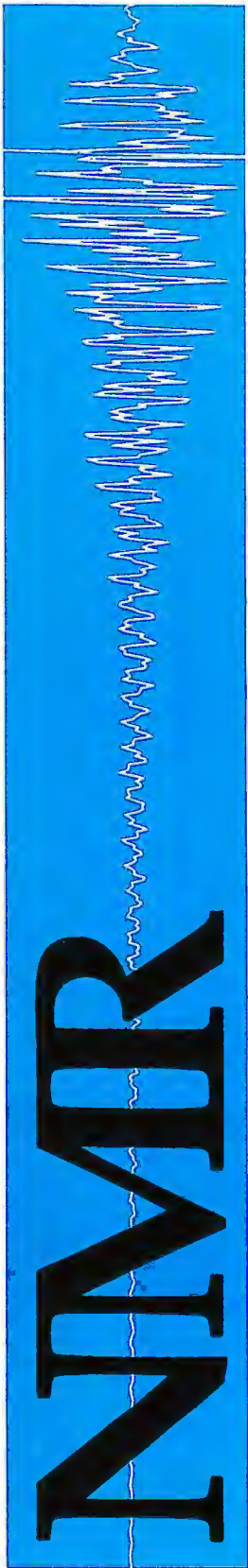
Bruker is well known for its leadership in high resolution NMR sample changer technology, with an unsurpassed record of over 500 units delivered. The great flexibility of the hardware, which has a capacity of 60 samples (standard) or 120 samples (optional), and the correspondingly powerful automation software make the Bruker sample changer ideal for highly automated NMR sites that require maximum throughput.

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March 6, 1995  
(received 3/16/95)

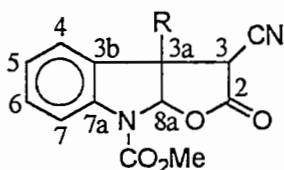
Dr. Bernard L. Shapiro  
Editor/Publisher  
TAMU NMR Newsletter  
966 Elsinore Ct.  
Palo Alto, CA 94303 USA

 **$^1\text{H}$  NMR Study of Tetrahydrofuro[2,3-b]indoles**

Dear Professor Shapiro:

In continuation of our studies<sup>1,2</sup> on the Grignard addition of alkylmagnesium halides to substituted 2-hydroxyindolenines, we recently synthesized a series of tetrahydrofuro[2,3-b]indoles substituted at C-3a by Me, Et, *i*-Pr or *t*-Bu (1-4). The  $^1\text{H}$  NMR spectra reveal some interesting features. Compounds 1-3 exist in both  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$  solvents as pairs of *cis-trans* diastereomers (with respect to C3a-alkyl and CN groups), in a ratio of 1:2 and 1:4, respectively (see figure), whereas the spectra of 4 in both solvents show only a single set of peaks attributed to the diastereomer carrying the *t*-Bu and CN groups in a *trans* orientation. In  $\text{CD}_3\text{OD}$  a fast H/D exchange takes place at the C-3 methine position for 1-3. The line broadening of the signals owing to H-7, H-8a and  $\text{CO}_2\text{Me}$  in the less polar solvent  $\text{CDCl}_3$  for 1-4 indicate the existence of a restricted rotation about the N- $\text{CO}_2\text{Me}$  bond. Finally, the non equivalence of the methylene protons ( $\text{ABX}_3$  spin system) in 2 ( $\text{R}=\text{Et}$ ) and the methyl groups in 3 ( $\text{R}=\textit{i}$ -Pr) reflect the chirality of these compounds.

Table.  $^1\text{H}$  NMR Chemical Shifts (ppm) for tetrahydrofuro[2,3-b]indoles (1-4) in  $\text{CDCl}_3$ .



- 1 R = Me  
2 R = Et  
3 R = *i*-Pr  
4 R = *t*-Bu

Comp.	H-3	H-4	H-5	H-6	H-7	H-8a	$\text{CO}_2\text{Me}$
1 <i>trans</i>	4.06(s)	7.64(d)	7.21(td)	7.41(td)	7.83(b)	6.26(b)	3.96(b)
1 <i>cis</i>	4.03(s)	7.64(d)	7.17(td)	7.38(td)	7.83(b)	6.30(b)	3.96(b)
2 <i>trans</i>	4.14(s)	7.64(d)	7.21(td)	7.42(t)	7.86(b)	6.28(b)	3.95(b)
2 <i>cis</i>	4.05(s)	7.64(d)	7.17(td)	7.39(t)	7.86(b)	6.33(b)	3.95(b)
3 <i>trans</i>	4.15(s)	7.68(d)	7.21(td)	7.44(td)	7.93(b)	6.26(b)	3.95(b)
3 <i>cis</i>	4.02(s)	7.68(d)	7.17(td)	7.40(td)	7.93(b)	6.37(b)	3.95(b)
4 <i>trans</i>	4.32(s)	7.78(d)	7.21(td)	7.44(t)	7.95(b)	6.37(b)	3.95(b)

Substituent chemical shifts (*trans, cis*): 1 1.67(s), Me, 1.72(s) Me; 2 2.06, 1.94(2dq)  $\text{CH}_2$ , 2.18, 2.08(2dq)  $\text{CH}_2$ , 0.92(t), Me, 0.88(t) Me; 3, 2.21(sept) CH, 2.62(sept) CH; 1.15, 0.80(2d) 2Me, 1.13, 0.74(2d) 2Me; 4 1.06(s) 3Me.

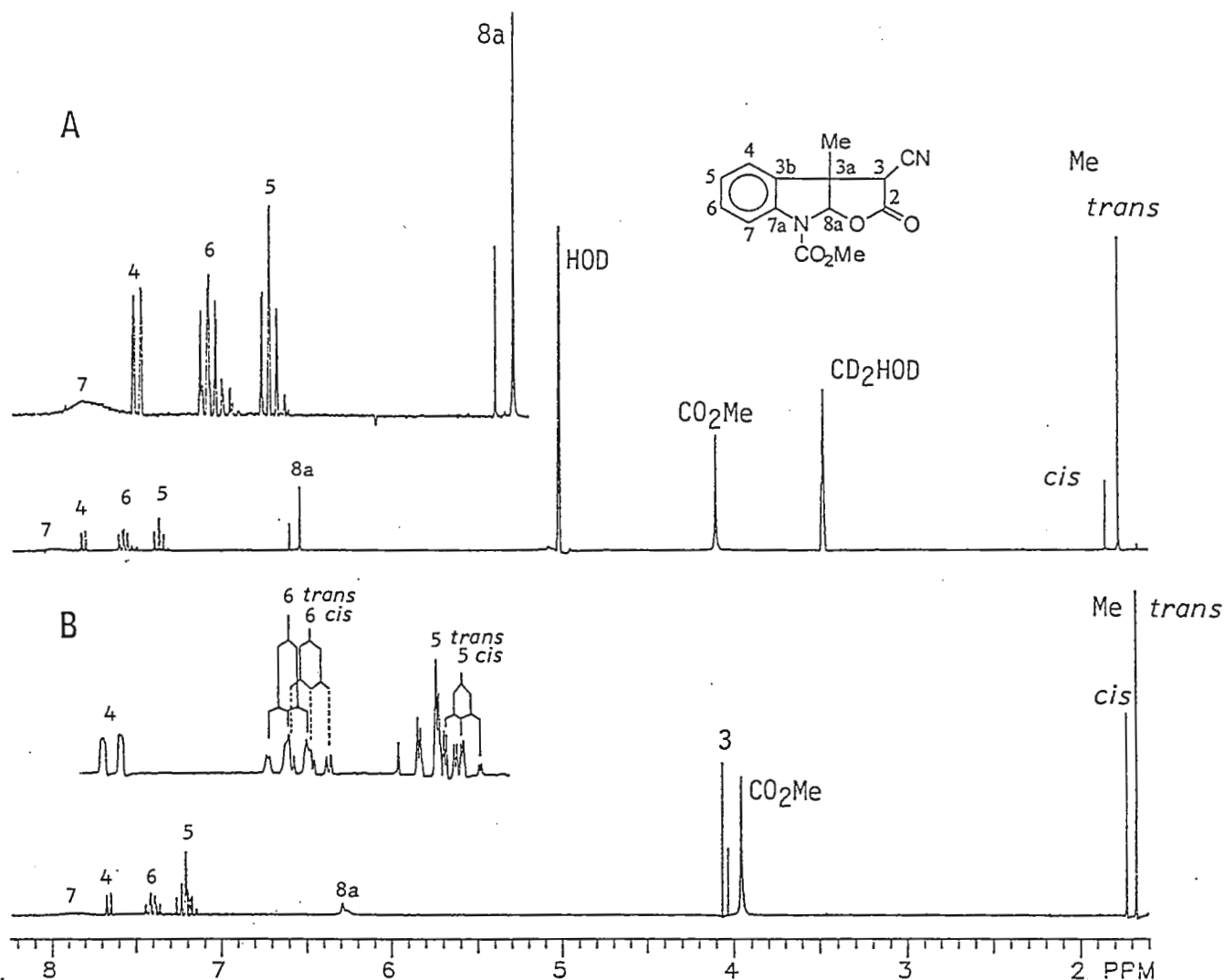

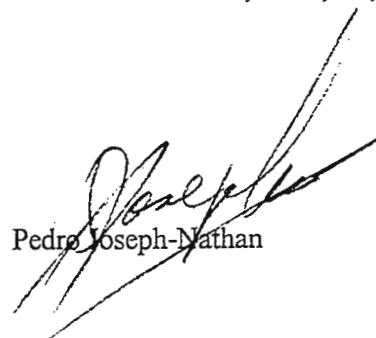


Figure. 300 MHz <sup>1</sup>H NMR spectra of 1. A) in CD<sub>3</sub>OD; B) in CDCl<sub>3</sub>.

1. Morales-Ríos, M.S.; Bucio, M.A.; Joseph-Nathan, P. *Tetrahedron Lett.*, 1994, 35, 881-882.
2. Morales-Ríos, M.S.; Bucio, M.A.; García-Martínez, C.; Joseph-Nathan, P. *Tetrahedron Lett.*, 1994, 35, 6087-6088.

Sincerely yours,

  
Martha S. Morales-Ríos

  
Pedro Joseph-Nathan

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

March 20, 1995  
(received 3/23/95)

Dear Barry:

### Superconductive high resolution probe

Varian and Conductus, a leading manufacturer of superconductive electronics, have been collaborating to investigate the sensitivity improvements which can be realised by using superconductive coils in a high resolution NMR probe. For a given magnetization, the sensitivity of an NMR probe is proportional to  $\eta\sqrt{Q/T}$  where  $\eta$  is the filling factor,  $Q$  is the quality factor of the coil and  $T$  is its temperature. Superconductive probes offer the possibility of very high  $Q$  coupled with operation at low temperature and therefore hold the promise of significant sensitivity improvement. The potential benefit of a cooled high resolution probe using normal metal coils has been demonstrated previously by Styles *et. al.* (1) for  $^{13}\text{C}$ , and superconductive probes have shown substantial sensitivity improvement in imaging applications (2). For high resolution applications, the superconductive coil must have good properties at high field, it must be possible to achieve a reasonable filling factor and the probe geometry must be sufficiently symmetric to maintain good field homogeneity.

We have made self resonant coils from thin films of the high temperature superconductor YBCO which, in zero magnetic field, has a transition temperature of 87K. The superconductor is deposited on a planar substrate and the coils are patterned by standard photolithographic techniques to a size similar to that of normal high resolution probe coils. Figure 1 shows the unloaded  $Q$  vs temperature for a coil with a resonant frequency of 465MHz in zero magnetic field and in a field of 11T (with the field parallel to the plane of the coil). Even in high field, the  $Q$  remains very high at temperatures below about 50K. For use as a transmitter in a pulsed FT experiment, coils must be able to carry a substantial rf current. We have investigated the current carrying capacity of these coils and, while there are significant non-linear effects, rf currents up to 4A can be carried. This is sufficiently high to generate short pulses, at least for a proton FT experiment.

Encouraged by these measurements, we have constructed a prototype probe using superconductive coils both for proton observe and for deuterium lock. Figure 2 shows the spectrum from a 5mm sample of 0.1% ethylbenzene at 400MHz with a signal-to-noise ratio of >1500:1, approximately three times the sensitivity which can be achieved with the same sample in a conventional probe. The coils were cooled to 25K using flowing helium and noise from the receiver was reduced by cooling the preamplifier in liquid nitrogen. Additional experiments to characterize the performance of the probe for more interesting applications are in progress.

- (1) P.Styles, N.F.Soffe, C.A.Scott, D.A.Cragg, F.Row, D.J.White and P.C.J.White, *J. Magn. Reson.* **60**, 397 (1984)
- (2) R.D.Black, T.A.Early, P.B.Roemer, O.M.Mueller, A.Mogro-Campero, L.G.Turner and G.A.Johnson, *Science*, **259**, 793 (1993)

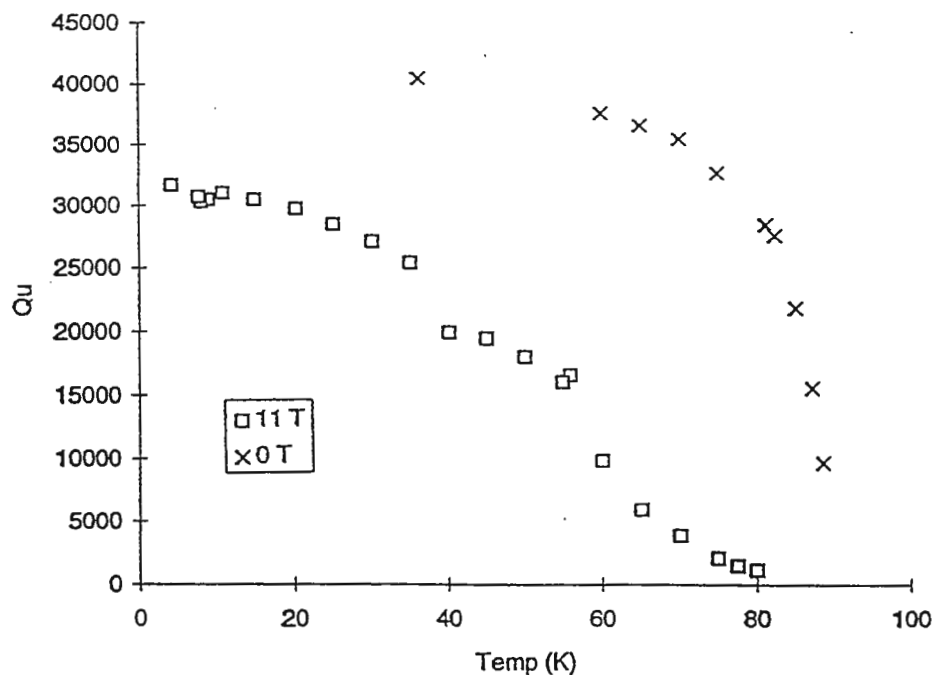


Fig. 1

Unloaded  $Q$  vs temperature for a superconducting coil in zero field and in an 11T field.

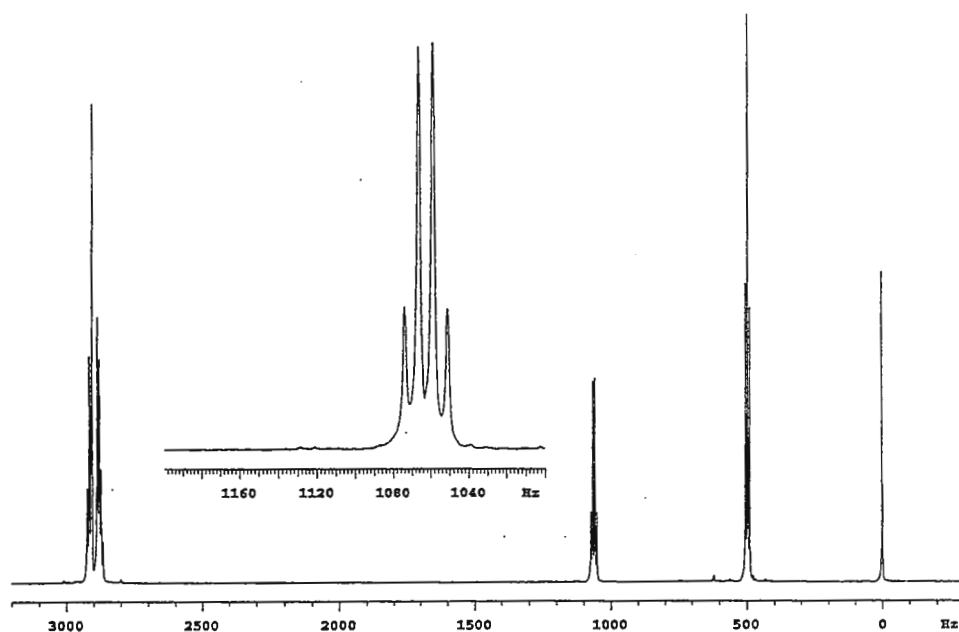


Fig. 2

400MHz spectrum of a 5mm sample of 0.1% ethylbenzene. S/N > 1500:1

We would like to thank our colleagues at Conductus for their continuing efforts on this project.

Kindest regards,

*Howard*

Howard Hill

*Wes*

Wes Anderson



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40%	p-Dioxane in Benzene-d <sub>6</sub> (min. 99.9%D)	<sup>13</sup> C	Sensitivity/ Resolution
0.05%	Trifluorotoluene in Benzene-d <sub>6</sub> (min. 99.6%D)	<sup>19</sup> F	Sensitivity
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Dr. B. L. Shapiro  
NMR Newsletter  
966 Elsinore Court  
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March 22, 1995  
(received 3/24/95)

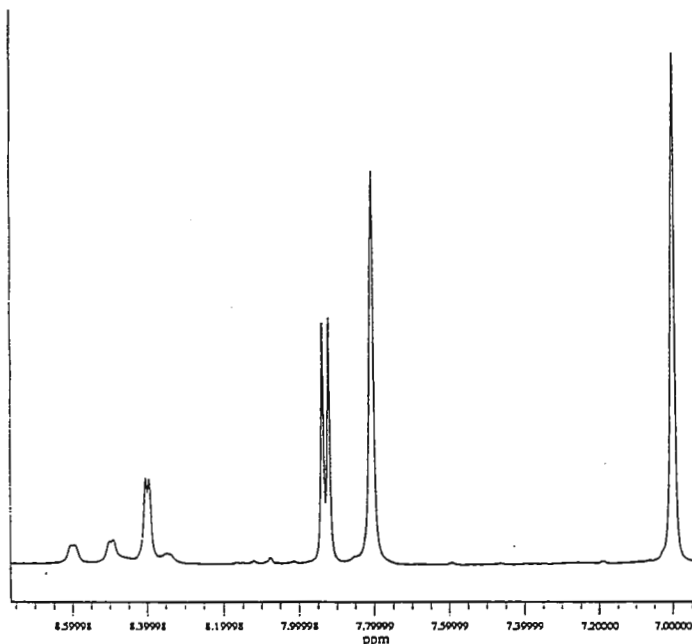
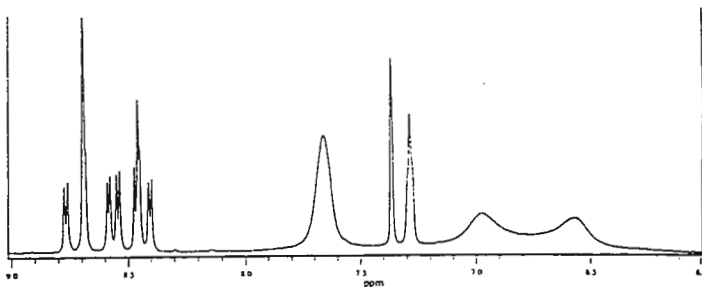
**Re: N-Ac-AKRHRKV-- A Conformational Change  
Upon Deprotonation of the Central Histidine**

Dear Barry

The N-terminal region of the histone protein H4 contains an unusual sequence of five amino acids which may serve as a binding locus for anionic modifiers of histone protein tertiary structure or nucleic acid binding. We have shown earlier that the histidine in this sequence is involved in phosphate binding especially above  $\text{pH} > 6.2$ , the  $\text{pK}_a$  of the histidine sidechain. Others have shown that this sequence is essential for some gene regulation events; e.g., mutations in this region of H4 derepress the yeast silent mating locus HML. For this reason we have used 500 MHz NMR to explore the conformational properties of N-acetyl-AKRHRKV as a function of pH and added anions, especially phosphate.

Even though the peptide is quite short, the assignment of all proton resonances is complicated because there are two lysines and two arginines within the same short peptide so that assignments cannot be based on chemical shift information alone. The redundant amino acids are not chemically equivalent and their amide NH,  $\alpha$ -H and side chain proton resonances have different chemical shift values. The assignments of the amide resonances were made by correlating each NH line with the corresponding  $\alpha$ -H line of the same amino acid residue by either TOCSY or COSY methods. The  $\alpha$ -H lines of Ala, His and Val can be related to unique  $\beta$ -H and other side chain resonances by TOCSY spectra. The two Lys and Arg spin systems can be assigned to specific amino acids (e.g. K2 vs K6) only by establishing NOESY connections between the Lys  $\alpha$ -amide NH lines and the  $\alpha$ -H resonances of the amino acids preceeding it (e.g. A1 vs R5). All seven amide peaks can be unambiguously assigned in the following downfield spectrum for 22 mg/mL peptide in 90%  $\text{H}_2\text{O}$ , 10%  $\text{D}_2\text{O}$ , pH 3.33, 5°C. A NOESYPHY spectrum failed to show any NH-NH cross peaks ruling out an  $\alpha$ -helix secondary structure at pH 3.33 and the  $^3\text{J}_{\text{NH}-\alpha\text{H}}$  couplings were found to be 6.5 to 7.0 Hz as opposed to 9 Hz for  $\beta$  structures. Furthermore a turn of any type would also require through-space interactions involving amide protons. None were found. These observations and the likely repulsions from positive charges on five adjacent residues forces us to conclude that the heptamer adopts a random coil conformation at pH 3.33.

The situation becomes more interesting at pH 7.30. At this pH peaks due to the side chain amino groups of lysine and arginine disappear and most of the amide resonances are broadened. There is a marked upfield shift (from 8.45 ppm at pH 3.33 to 7.97 ppm at pH 7.30) of the valine amide resonance following deprotonation of the C-terminal carboxyl group, indicating a significant change in the environment of this amide proton. This conclusion is reinforced by other observations. The  $^3J_{\text{NH}-\alpha\text{H}}$  of valine increases from 6.5 to 9 Hz and its amide proton exchange rate does not increase with base like the other amide protons. The valine amide proton is the only sharp doublet at pH 7.30 implying hydrogen bonding to a carbonyl in the peptide chain. The most likely candidate is the histidine carbonyl because there are pronounced NOEs between the histidine H2 proton and the  $\alpha$ - and  $\beta$ -protons of valine. Thus a loop is formed at the C-terminal end of this peptide at pH 7.30. Other interesting changes were observed when phosphate is added to the peptide but that is a story we will tell elsewhere.



Hai Minh Vu

and

Mike Minch\*



Department of Chemistry

March 7, 1995

(received 3/15/95)

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

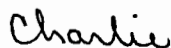
Dear Barry,

### Steric Effects on $^{13}\text{C}$ NMR Chemical Shifts

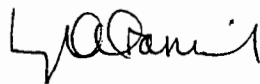
Recently, we have synthesized and characterized two series of Group 13 metal adducts of secondary amines,  $\text{Me}_3\text{M-HR}$ , [ $\text{M} = \text{Ga}, \text{In}$ ] for comparison with our previously reported series  $\text{Me}_3\text{Al-HR}$ , [*Polyhedron* **12**, 389 (1993)]. Here  $\text{R} = \text{NMe}_2$  (**1**);  $\text{NEt}_2$  (**2**);  $\text{NPr}^n_2$  (**3**);  $\text{NPr}^i_2$  (**4**);  $\text{NBu}^n_2$  (**5**);  $\text{NBu}^i_2$  (**6**);  $\text{NBu}^s_2$  (**7**);  $\text{N}(\text{CH}_2\text{Ph})_2$  (**8**);  $\text{N}(\text{c-C}_6\text{H}_{11})_2$  (**9**);  $\text{NC}_4\text{H}_8$  (**10**);  $\text{NC}_5\text{H}_{10}$  (**11**);  $\text{NC}_6\text{H}_{12}$  (**12**);  $\text{N}(\text{CH}_2\text{CH}_2)_2\text{NMe}$  (**13**). A comparison of the  $^{13}\text{C}$  NMR spectral data for the adducts, parent amines and  $\text{Me}_3\text{M}$  gives insight into the influence of steric interactions and the nature of the metal on the chemical shift values. In the case of the methyl groups on Al, Ga, and In, the  $^{13}\text{C}$  chemical shifts are upfield from TMS for the adducts and are dependent upon the metal and the steric demands of the amine moiety. For any particular amine, the order of increasing downfield  $^{13}\text{C}$  chemical shift is  $\text{Al} < \text{Ga} < \text{In}$ . Also, in each series, the methyl  $^{13}\text{C}$  chemical shifts are shifted downfield with the general increasing steric demands on the amine. For example, with  $\text{HNMe}_2$  (**1**), the  $\delta_c$  values are most negative, followed by the cyclic secondary amines (**10-13**), then the amines containing secondary carbons at C(1) position (**2, 3, 5, 6, and 8**) and finally those containing tertiary C(1) carbons (**4, 7, and 9**).  $^{13}\text{C}$  NMR chemical shifts are known to be very sensitive to steric effects [*Stothers, Carbon - 13 NMR Spectroscopy*, 1972.]

Finally, in order to correlate the  $^{13}\text{C}$  NMR chemical shift data with amine steric size, we have used amine cone angle ( $\theta$ ) data for the free amine. Available cone angle data versus  $\text{Me-M}$  ( $\text{M} = \text{Al}, \text{Ga}, \text{In}$ )  $^{13}\text{C}$  NMR chemical shift values, which are plotted in the figure for the three homologous adduct series, indicates a greater downfield  $^{13}\text{C}$  chemical shift with increasing amine cone angle, with the  $\text{Bu}^i$ ,  $\text{Bu}^s$ , and  $\text{CH}_2\text{Ph}$  derivatives being exceptions. For the latter, the  $^{13}\text{C}$  shift data imply that the effective cone angles in the amine moieties of **6, 7, and 8** are much less (ca.  $125^\circ$ ,  $134^\circ$ , and  $127^\circ$ , respectively) than the calculated values for the free amines ( $138^\circ$ ,  $158^\circ$ , and  $140^\circ$ ). This suggests that the cone angles of these amines, by analogy to phosphines that have large internal degrees of freedom, may decrease under steric strain.

Sincerely,



Charles L. Watkins  
Professor



Larry K. Krannich  
Professor and Chairman

## Amine Cone Angle Versus C13 NMR Chemical Shift

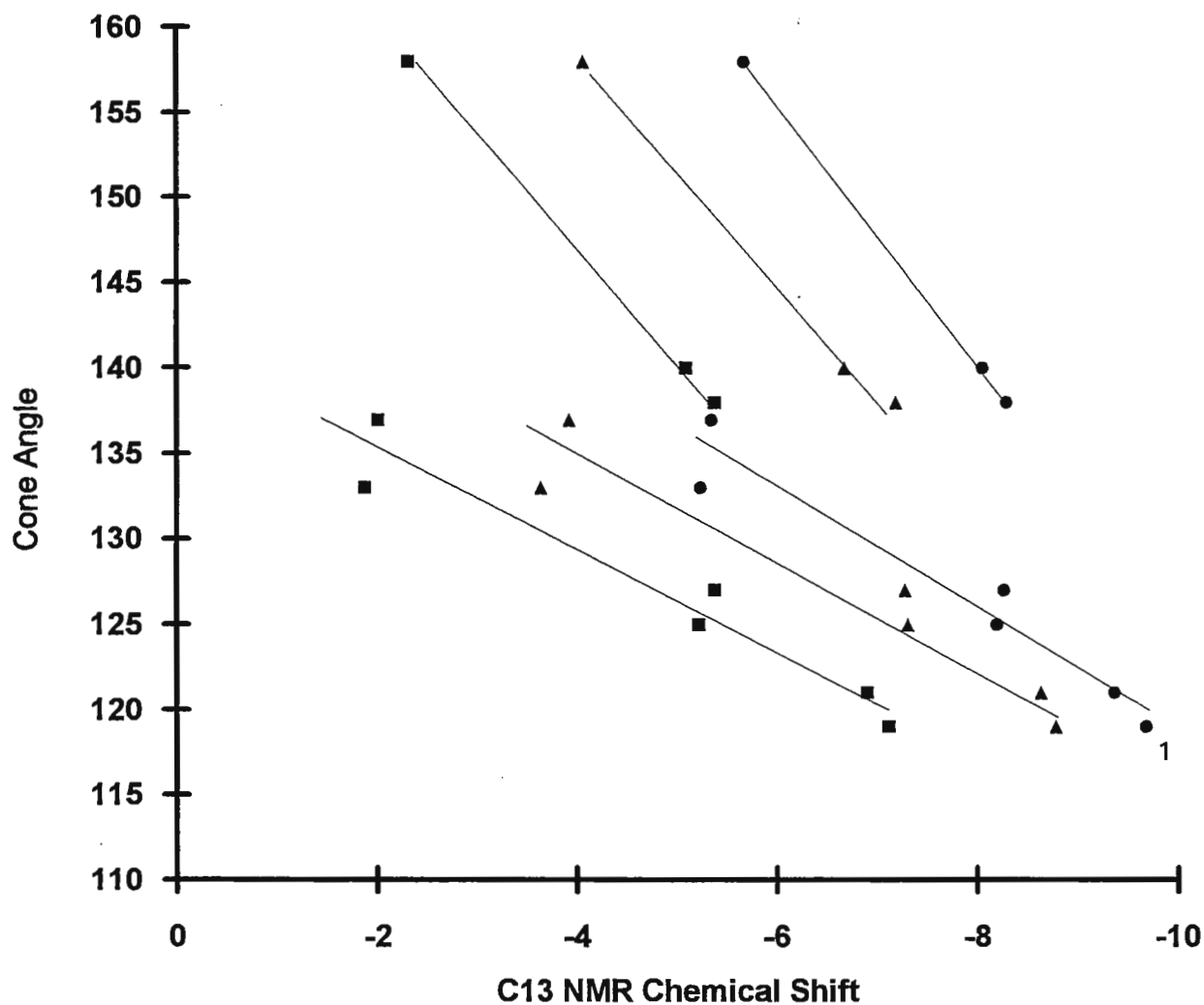


Figure. M-Me C-13 NMR chemical shifts (ppm, TMS) for the Me<sub>3</sub>Al- (●), Me<sub>3</sub>Ga- (■), and Me<sub>3</sub>In- (▲) amine adducts as a function of amine cone angle ( $\theta$ ). Compounds in order of increasing cone angle are 1, 11, 2, 3, 9, 4, 6, 8, 7.

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Albuquerque, New Mexico 87185-0367

February 14, 1995

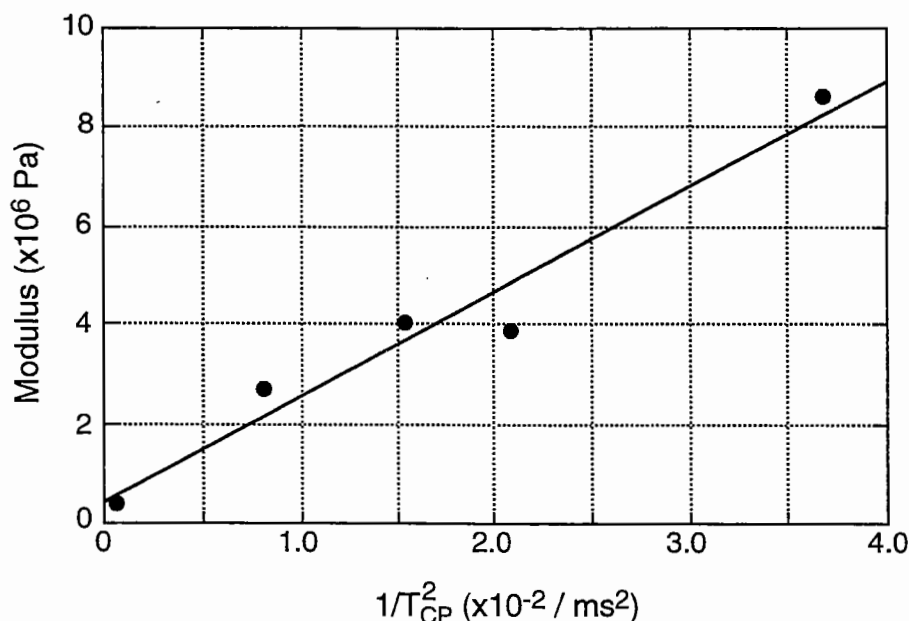
(received 2/27/95)

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

Dear Barry,

**Relationship Between the Modulus and Cross Polarization  
Time of a Filled Silicone**

An ongoing research project at Sandia involves investigating the structure-property relationships of composite materials composed of a polydimethylsiloxane (PDMS) matrix reinforced with silica fillers. In an attempt to correlate NMR data with mechanical data,  $^{29}\text{Si}$  cross polarization (CP) MAS NMR was used to investigate the effect of the filler on the behavior of the matrix phase of these materials. Depending on the amount and the type of silica filler, the polymer matrix can vary from mobile to semi-rigid. Optimizing and maintaining a stable Hartman-Hahn match for mobile samples can be difficult. To reduce this problem, we used a variable-amplitude CP (VACP) experiment with a ramp function during the contact time, a method developed by Peerson and coworkers for problems associated with high-speed MAS.<sup>1</sup> The VACP experiment improves the cross polarization efficiency considerably, although the intensity of the signal from the mobile phase is still not quantitative.

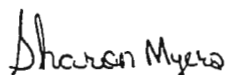


Relationship between the moduli and cross polarization times for a series of filled silicones.

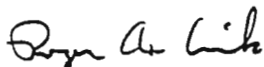
This work is supported by the United States Department of Energy under Contract DE-AC04-94AL85000.

For a series of PDMS composites, the cross polarization time constant ( $T_{CP}$ ) for the polymer varied from 5 ms to 40 ms. These results show that the mobility of the polymer matrix is affected by the type of filler used. In order to understand polymer structure-property relationships, Marcinko and coworkers developed a model for correlating  $T_{CP}$  with the modulus for a series of polyurethane elastomers.<sup>2</sup> They predicted a linear relationship between the modulus and  $1/T_{CP}^2$  of the material. Using these principles, we wanted to determine if the same correlation exists for a filled material. The modulus plotted against the reciprocal of  $T_{CP}^2$  for these materials (Figure) shows the expected linear relationship. These preliminary results are encouraging and hopefully will aid in estimating the modulus for materials which are too rigid or too soft for mechanical measurements.

Sincerely,



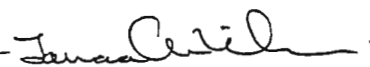
Sharon A. Myers



Roger A. Assink



Eric Black<sup>3</sup>



Tamara Ulibarri

<sup>1</sup> O. B. Peerson, X. Wu, I. Kustanovich, and S. O. Smith *J. Magn. Reson. Series A*, **104**, 334 (1993).

<sup>2</sup> J. J. Marcinko, A. A. Parker, P. L. Rinaldi, W. M. Ritchey *J. Appl. Polym. Sci.*, **51**, 1777 (1994).

<sup>3</sup> Current Address: Georgia Pacific, 2883 Miller Rd., Decatur GA 30035

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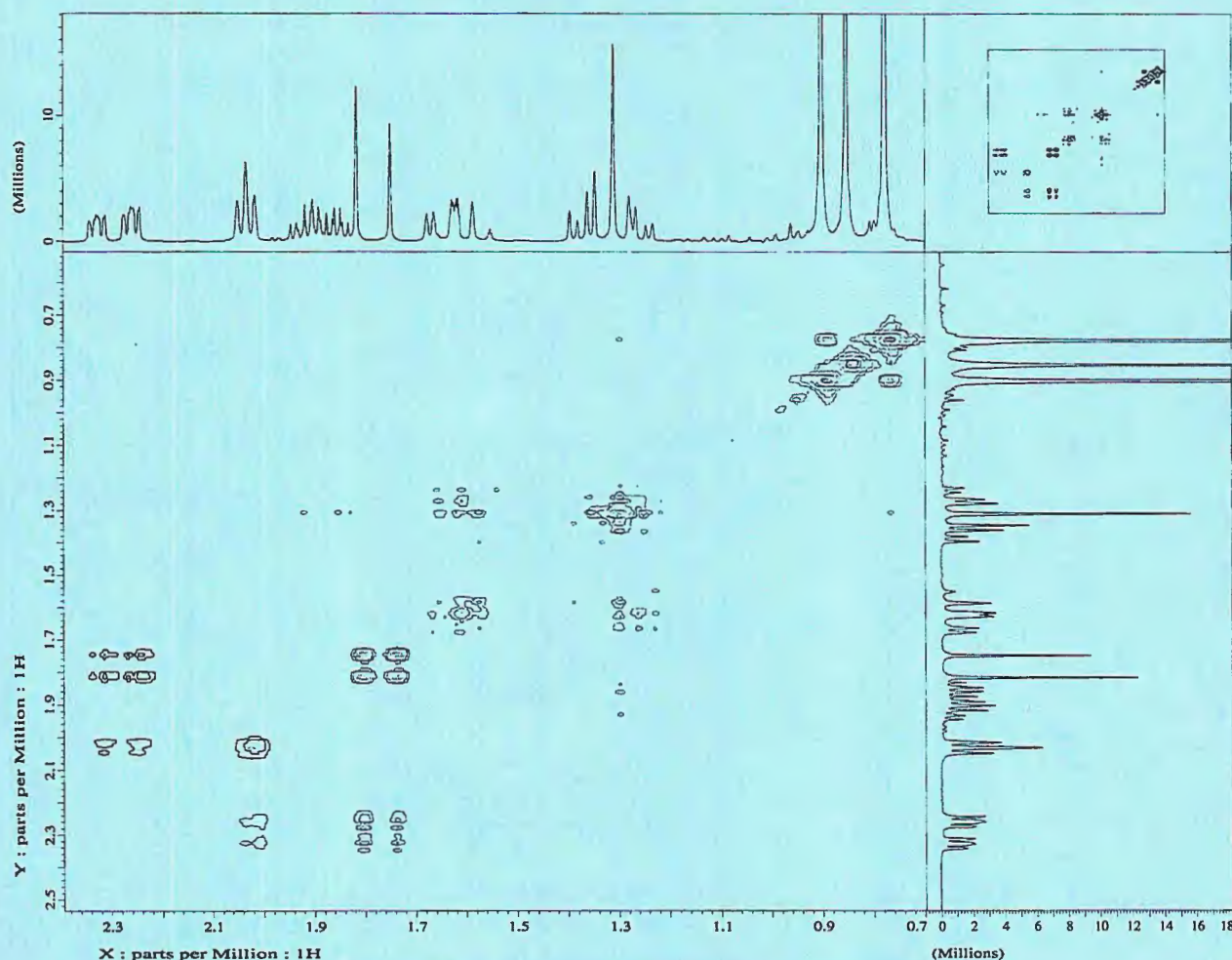
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