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# NMR

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**FORTHCOMING NMR MEETINGS**

**28th ENC (Experimental NMR Conference)** - April 5-9, 1987; Asilomar; Pacific Grove, California; Chairman: Dr. Lynn W. Jelinski, (AT&T Bell Laboratories); For information, contact Dr. Charles G. Wade, ENC Secretary, IBM Instruments, Inc., 40 West Brokaw Road, San Jose, California 95110, (408) 282-3641.

**8th International Meeting "NMR Spectroscopy"** - July 5-10, 1987; University of Kent at Canterbury, England; For information, contact Dr. John F. Gibson, Royal Society of Chemistry, Burlington House, London W1V 0BN, England.

**29th ENC (Experimental NMR Conference)** - April 17-21, 1988; Rochester, New York; Chairman: Professor Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, (215) 898-6459. For information, contact Dr. Charles G. Wade, ENC Secretary, IBM Instruments, Inc., 40 West Brokaw Road, San Jose, California 95110, (408) 282-3641.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence  
 Should be Addressed to:

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

**DEADLINE DATES**

No. 339 (December) --- 28 November 1986

No. 340 (January) ---- 26 December 1986

BIRKBECK COLLEGE  
*University of London*

Department of Chemistry  
01-580 6622

Malet Street  
London, WC1E 7HX

14 august 1986. (Received 26 September 1986)

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

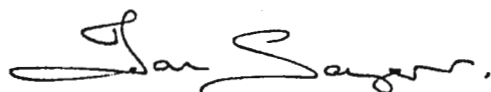
STATIC AND DYNAMIC MOLECULES IN DISORDERED SOLIDS

Dear Professor Shapiro;

We are studying the solid state NMR properties of sandwich molecules of the type  $[(C_6H_4X_2)Fe(C_5H_5)]^+[EF_6]^-$ , (X = H, E = P, As, Sb). The 75 MHz  $^{13}C$  CP-MAS NMR spectrum of compound I (X = H, E = As; Fig. 1) consists of a pair of equally intense benzene signals (Bz; 87 and 88 ppm) and a pair of equally intense cyclopentadienyl signals (Cp; 76 and 77 ppm). Although the width of the  $^{13}C$  resonance lines depends on the level of proton decoupling power, the downfield signals of each pair are always relatively broad with  $\Delta\nu^{1/2} \sim 50\text{Hz}$  (at  $^1H$  DP = 70KHz) compared to the upfield signals where  $\Delta\nu^{1/2} \sim 15\text{Hz}$ .

Previous studies<sup>1</sup> have shown that the monoclinic phase (265K to 305K) of I contains two different molecular sites (Fig. 1). The molecule in site 1 is disordered through rapid rotation ( $\tau_c \sim 10^{-9}$  sec. at 290K) whilst the molecule in site 2 is relatively static. Intuitively one would assign the the broad and narrow components of the spectrum to the static and dynamic molecules respectively, and this assignment was confirmed by introducing a 2 millisecond dipolar dephasing delay between the end of the CP contact and the start of the FID acquisition. The effect is to remove the broad components of the spectrum and hence to assign the broad signals to the more strongly coupled static molecules of the unit cell; the result is summarised in fig. 1. The motional characteristics of the monoclinic and cubic phases of compound I will be published in the near future.

Yours sincerely



Ian Sayer

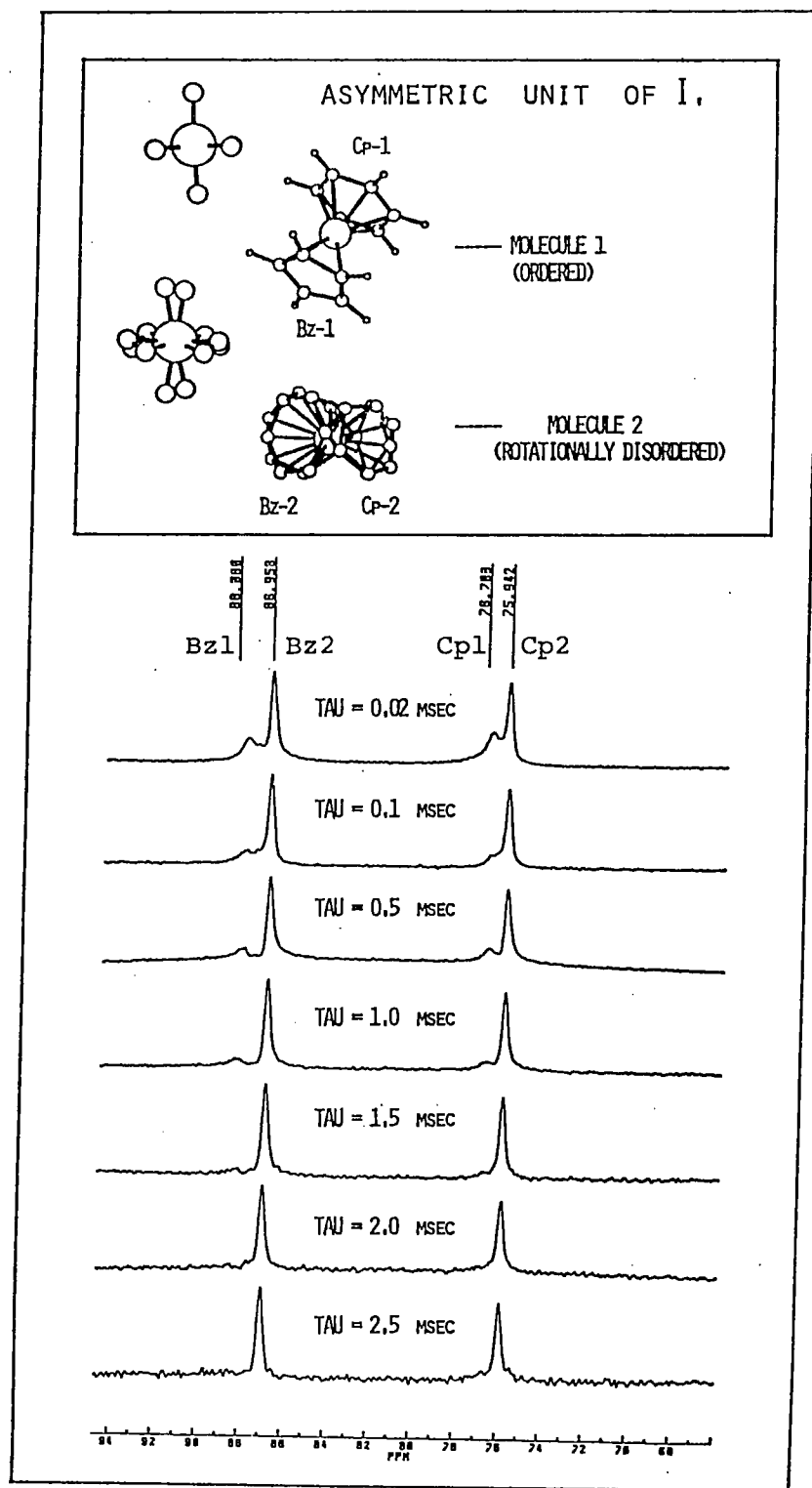


David B Davies

REFERENCE

- 1 I. Sayer, PhD Thesis, University of London 1985.

Fig. 1. Carbon-13 CP-MAS NMR spectra of compound I in the monoclinic phase. A dipolar dephasing delay TAU is introduced into the CP sequence causing dephasing of the downfield broad components of each pair of signals. Hence, the downfield component of the Cp and Bz signals can be assigned to the static molecules of the unit cell ( Bz-1/Cp-1 ) and the narrow upfield resonances can be assigned to the rotating molecules ( Bz-2/Cp-2 ).





337-4

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(215) CH 2-0400



August 28, 1986

(Received 19 September 1986)

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

P-31 NMR of Adsorbed DFP on Ion Exchange Resins

Dear Barry,

Recently we have become interested in monitoring the decomposition of diisopropyl fluorophosphate, DFP, on a variety of chemically modified ion exchange resins. DFP is a cholinesterase inhibitor and is highly toxic to the central nervous system. The ion exchange resins are commercially available styrene/divinyl benzene macro-reticular beads with and without strong acid sites. The normal method of studying these systems involves extraction techniques which are time consuming and often ambiguous.

Initially we started to characterize these adsorbed molecules using solid state NMR. We currently have a Doty Scientific broadband, double-tuned CPMAS probe for our Varian XL-200. We were quite surprised to find that the DFP is highly mobile on the surface of the ion exchange resin and looks essentially "liquid-like" on the NMR timescale. In fact, we were able to obtain reasonable spectra using our Varian solution probe by placing the dry beads in 10 mm tubes and acquiring data using a one pulse experiment. The linewidths were approximately 200 Hz without spinning or proton decoupling. As shown in the figure, we start with essentially pure DFP on the surface of the ion exchange resin (B) and over time it decomposes by hydrolysis (C,D,E). It is interesting to note that when DFP is loaded onto activated carbon it appears to become immobilized on the surface as evidenced by a 20-fold increase in the P-31 NMR linewidth to 5 kHz (F).

Further characterization of these samples is in progress using F-19 and solid state NMR.

Sincerely,

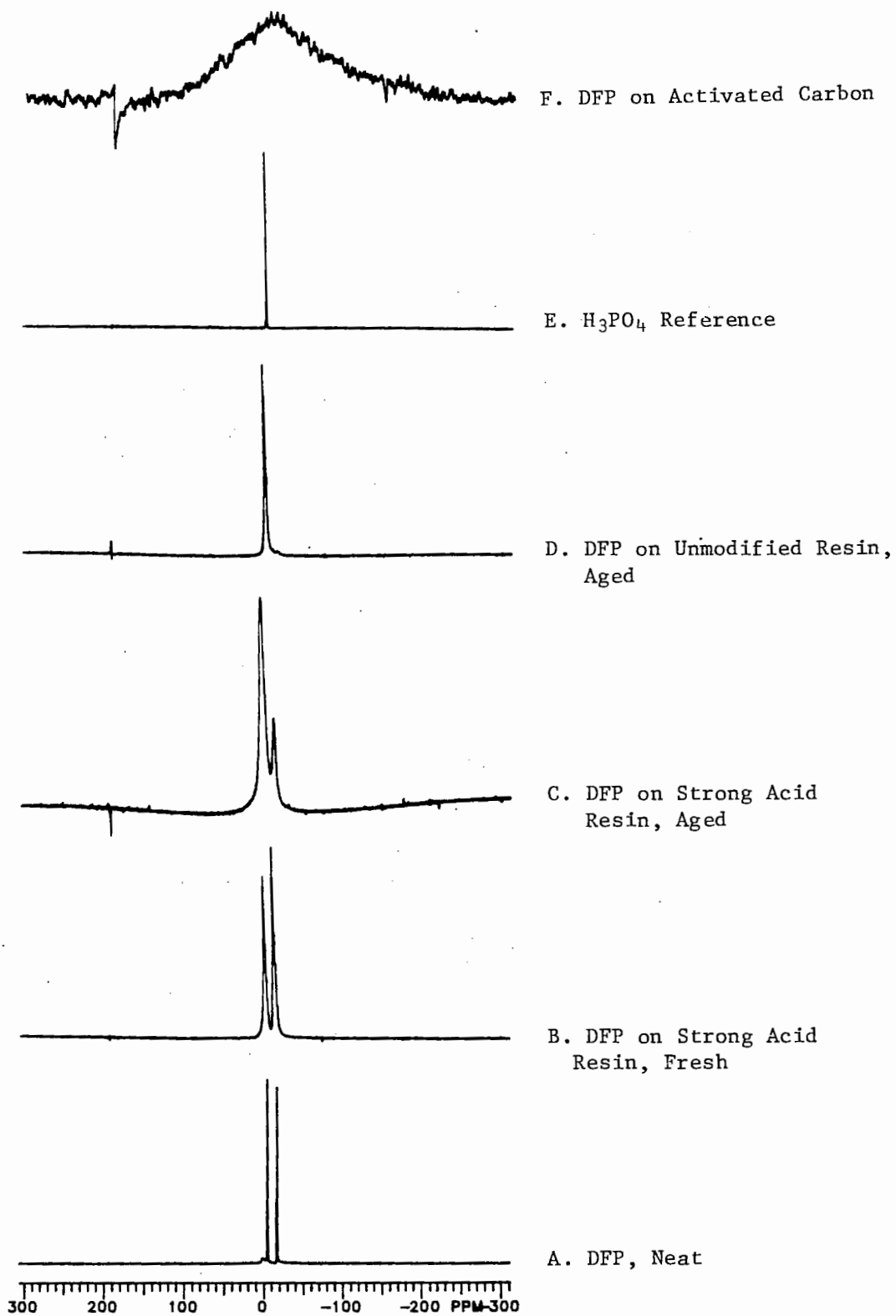
*Becky Smith*

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## THE UPJOHN COMPANY

KALAMAZOO, MICHIGAN 49001, U.S.A.  
TELEPHONE (616) 323-4000

August 15, 1986 (Received 28 August 1986)

Specific Deuteration in Proteins

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

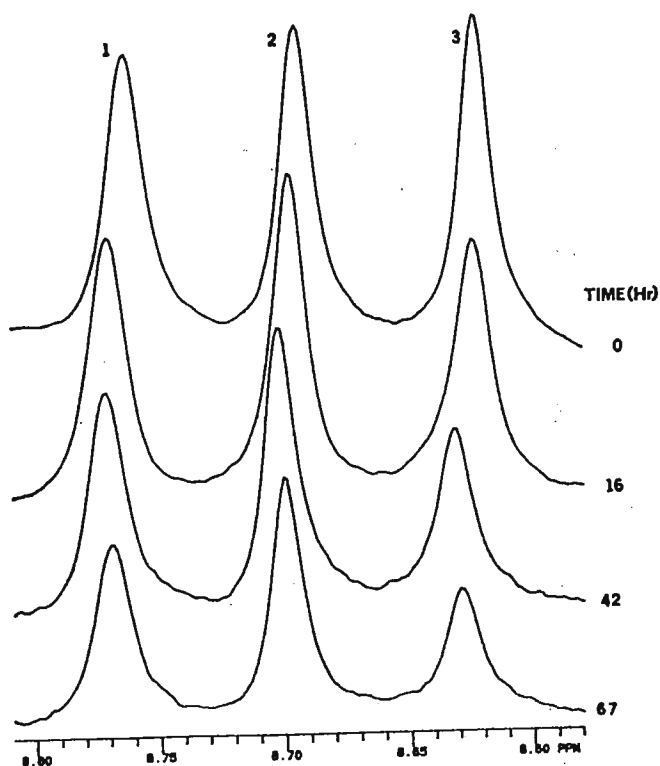
Dear Barry,

As an aid in the assignment of resonances in the complex spectra obtained from proteins in the 20 kDalton range, we are studying molecules enriched in  $^{13}\text{C}$ ,  $^{15}\text{N}$  and  $^2\text{H}$ . An example of the type of information to be gleaned in this manner is shown in Figure 1. This depicts a series of 400 MHz  $^1\text{H}$ NMR spectra of the imidazole ring C2 protons of the three histidine residues in pituitary bovine somatotropin ( $\text{MW} \approx 22$  kDaltons). These protons slowly exchange with deuterium at rates dependent on the solvent accessibility of the residues. The fastest exchanging proton is obviously 3, assigned to HIS-170 (in a separate experiment) with a first-order rate constant  $k$  of  $1.9 \times 10^{-6} \text{ s}^{-1}$ .

Yours sincerely,

*Neil MacKenzie*

Neil E. MacKenzie, Ph.D.





# MG-5DP Peak Reading Portable Laboratory Gaussmeter

---

## GENERAL:

The MG-5DP is a general purpose peak reading portable Hall effect gaussmeter designed to measure both DC & AC (RMS) magnetic fields.

Three full-scale bipolar ranges of  $\pm 100.0$  gauss,  $\pm 1.000$  KG and  $\pm 10.00$  KG with 100% over-range and resolution of 0.05% provides DC & AC field readings from  $\pm 100$  milligauss to  $\pm 19.99$  KG with true RMS readings from 3 Hz to 20 KHz; readings are displayed on a  $3\frac{1}{2}$  digit  $\pm 0.05\%$  bipolar LCD meter.

In the Peak Mode, the MG-5DP will sense and display the most recent peak magnetic field level from DC to 20KHz.

This instrument can be set to either detect the peak value when the field is bipolar (varying from positive to negative) or it can be set to exclusively detect either the positive peak or the negative peak of a varying field. Because of the unique digital circuit design, there is no decay in the peak field reading.

A wide selection of precalibrated transverse and axial Hall probes is available to meet most every application, including probes which will extend the measuring range of this instrument to 150.0 KG.

The MG-5DP operates either from AC or from sealed lead acid batteries. During AC operation, the batteries receive a floating charge which keeps them fresh until the instrument is required for portable use. Freshly charged batteries will continuously operate this instrument for approximately 10 hours.

In addition, analog outputs are also provided for simultaneous external monitoring of both the instantaneous field level and the peak field level.



---

## APPLICATIONS:

- Measure Residual Fields
- Analyze Magnetic Circuits and Components
- Classify Magnets
- Measure Absolute & Differential Fields
- Plot Field Uniformity
- Measure Stray & Leakage Fields

---

## FEATURES:

- Positive and/or negative peak reading
- $3\frac{1}{2}$  Digit  $\pm 0.05\%$  Bipolar Display
- DC & AC Fields,  $\pm 100$  milligauss to  $\pm 19.99$  KG with 1X probes
- Range Extendable to 150.0 KG with Select Probes
- Wide Selection of Precalibrated Probes: 1X, 10X & 100X
- True RMS Readings to 20 KHz
- Operates with either AC or Battery; Fully Portable

- Analog Outputs For External Monitoring
- No field decay in Peak Mode
- High Impact Plastic Case with Carrying Handle
- One Year Warranty

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## ACCESSORIES:

- **Precalibrated Hall Probes**  
A wide selection of 1X, 10X and 100X precalibrated Hall probes is available to meet most applications.
- **Zero Gauss Chamber (Model ZG-1)**  
A mu-metal shield used to shunt the earth's field around the Hall element in order to more accurately zero the gaussmeter when precise low field measurements are required.
- **Reference Magnets**  
Transverse and axial precision reference magnets are available when precise instrument calibration at a particular field is desirable.

# MG-5DP Peak Reading Portable Laboratory Gaussmeter

## SPECIFICATIONS:

Display (Digital): 3 1/2 digit  $\pm 0.05\%$  bipolar LCD—(Liquid Crystal Display)  
Range: 3 Full Scale Ranges:  
 $\pm 100.0$  gauss,  $\pm 1.000$  KG and  $\pm 10.00$  KG with 100%  
over-range ( $\pm 100$  milligauss to  $\pm 19.99$  KG)  
Resolution: (With 100% over-range)  
0.05% ( $\pm 100$  milligauss—100.0 Gauss Range,  $\pm 1$  Gauss—1.000 KG  
Range,  $\pm 10$  Gauss—10.00 KG Range)  
Instrument Accuracy (Less Probe): Temperature Range 10°–40°C.  
Meter Reading: 1,000 counts Full Scale with 100% over-range

Range Setting ..... DC Accuracy 0–100% FS  $\pm 1$  count  
100G .....  $\pm 0.075\% \pm 0.008\%/^{\circ}\text{C}$   
1KG .....  $\pm 0.075\% \pm 0.008\%/^{\circ}\text{C}$   
10KG .....  $\pm 0.075\% \pm 0.008\%/^{\circ}\text{C}$   
RMS Accuracy 1% to 100% FS  $\pm 1$  count  
100G (3 Hz to 5 KHz) .....  $\pm 2\%$  (3 Hz–10 Hz),  
 $\pm 1\%$  (10 Hz–5 KHz)  $\pm 0.1\%/^{\circ}\text{C}$   
1KG (3 Hz to 20 KHz) .....  $\pm 1\%$  (3 Hz–10 Hz),  
 $\pm 0.3\%$  (10 Hz–20 KHz)  $\pm 0.1\%/^{\circ}\text{C}$   
10KG (3 Hz to 20 KHz) .....  $\pm 1\%$  (3 Hz–10 Hz),  
 $\pm 0.3\%$  (10 Hz–20 KHz)  $\pm 0.1\%/^{\circ}\text{C}$   
Peak Meter Reading Accuracy: (0 to  $\pm 1999$  count max.)  $\pm 1\%$  of full scale  
 $\pm 1$  count

Analog Output:  $\pm 2.000\text{V}$  Full Scale: 2 KOHM Minimum Load Impedance  
Range Setting ..... DC Accuracy 100% FS  
100G .....  $\pm 0.025\% \pm 0.006\%/^{\circ}\text{C}$   
1KG .....  $\pm 0.025\% \pm 0.003\%/^{\circ}\text{C}$   
10KG .....  $\pm 0.025\% \pm 0.002\%/^{\circ}\text{C}$

AC Frequency ..... Output Voltage  
100G ..... 0.2dB–5 KHz, 2dB–10 KHz, 5dB–20 KHz, 10dB–20 KHz, 10dB–20 KHz  
1KG ..... 1  $\mu\text{V}$   
10KG ..... 0.2  $\mu\text{V}$

Peak Analog Output Accuracy: (0 to  $\pm 2.000\text{V}$  max.) 1% of full scale  
Peak Reading Resolution: (10°C – 40°C) from DC to 20 KHz (sinewave),  
minimum pulse width 50  $\mu\text{sec}$  (square wave)  
Range ..... Peak ..... Slew Rate  
100 G ..... 1 Gauss ..... 25 G/ $\mu\text{sec}$  (max.)  
1 KG ..... 10 Gauss ..... 250 G/ $\mu\text{sec}$   
10 KG ..... 100 Gauss ..... 2.5 KG/ $\mu\text{sec}$

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Net Weight: 4.75 lbs.—2.2 kg Shipping Weight: 6.0 lbs.—2.7 kg

## HALL PROBES

	Model	% Linearity of Reading	Temperature Coefficient %/ $^{\circ}\text{C}$	Temperature Range $^{\circ}\text{C}$	Style	L	Stem Size x W x T	Active Area L x W
TRANSVERSE	HP-14S	$\pm 1\%$ to 20 KG	–0.1	–55 to +100	V-1X	0.5" (12.7 mm)	0.25" (6.35 mm)	.040" x .080" (1 x 2 mm)
	HP-145S				I-1X	4" (10.16 cm)	0.155" (3.94 mm)	.043" (1.09 mm)
	HP-145F	$\pm 1\%$ to 20 KG	–0.1	–55 to +100	II-1X	4" (10.16 cm)	0.165" (4.19 mm)	.053" (1.35 mm)
	HP-145R				I-1X	4" (10.16 cm)	0.175" (4.45 mm)	.063" (1.60 mm)
	HP-345S- ( )	$\pm 0.25\%$ to 10 KG (-10)			I-10X	4" (10.16 cm)	0.155" (3.94 mm)	.043" (1.09 mm)
	HP-345F- ( )	$\pm 0.5\%$ to 20 KG (-20) / (Specify)	–0.04	–40 to +100	II-10X	4" (10.16 cm)	0.165" (4.19 mm)	.053" (1.35 mm)
	HP-345R- ( )	$\pm 1\%$ to 30 KG (-30)			I-10X	4" (10.16 cm)	0.175" (4.45 mm)	.063" (1.60 mm)
	HP-645S				I-100X	4" (10.16 cm)	0.155" (3.94 mm)	.043" (1.09 mm)
	HP-645F	$\pm 0.1\%$ to 30 KG	$\pm 0.005$	–40 to +100	II-100X	4" (10.16 cm)	0.165" (4.19 mm)	.053" (1.35 mm)
	HP-645R				I-100X	4" (10.16 cm)	0.175" (4.45 mm)	.063" (1.60 mm)
AXIAL	HP-1145S				I-100X	4" (10.16 cm)	0.155" (3.94 mm)	.043" (1.09 mm)
	HP-1145F	$\pm 1\%$ to 30 KG / $\pm 1.5\%$ to 150 KG	$\pm 0.005$	–40 to +100	II-100X	4" (10.16 cm)	0.165" (4.19 mm)	.053" (1.35 mm)
	HP-1145R				I-100X	4" (10.16 cm)	0.175" (4.45 mm)	.063" (1.60 mm)
	HP-24S	$\pm 1\%$ to 20 KG	–0.1	–55 to +100	V-1X	0.5" (12.70 mm)	0.25" (6.35 mm)	.040" x .080" (1 x 2 mm)
	HP-245S				III-1X	5.0" (12.70 cm)	0.268" (6.35 mm)	.040" x .080" (1 x 2 mm)
	HP-245F	$\pm 1\%$ to 20 KG	–0.1	–55 to +100	IV-1X			
	HP-845S- ( )	$\pm 0.25\%$ to 10 KG (-10)	–0.04	–40 to +100	III-10X	9.0" (22.86 cm)	0.263" (6.68 mm)	.040" Dia (1 mm)
	HP-845F- ( )	$\pm 0.5\%$ to 20 KG (-20) / (Specify)			IV-10X			
	HP-1045S	$\pm 0.25\%$ to 30 KG	$\pm 0.005$	–40 to +100	III-100X	9.0" (22.86 cm)	0.263" (6.68 mm)	.020" Dia (0.5 mm)
	HP-1045F				IV-100X			
	HP-1245S	$\pm 1\%$ to 30 KG / $\pm 1.5\%$ to 150 KG	$\pm 0.005$	–40 to +100	III-100X	9.0" (22.86 cm)	0.263" (6.68 mm)	.020" Dia (0.05 mm)
	HP-1245F				IV-100X			

(Note: Thickness of standard probe applies to 1/2" from tip only)

Model Number Suffix S—Standard F—Flexible R—Ruggedized

Note: The above listing is representative of our most widely used probes. Please consult us if your application requirements cannot be met by one of these probes.

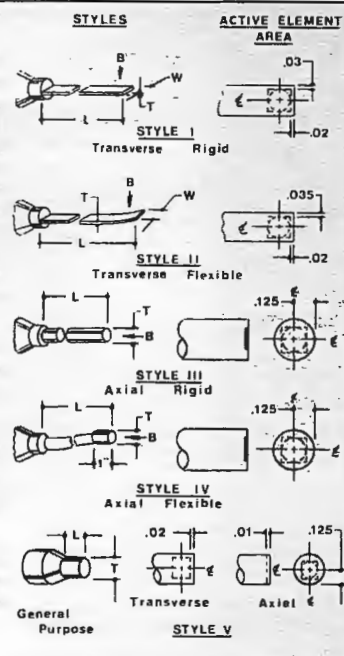
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Uppsala 5 September 1986

(Received 15 September 1986)

Professor B.L. Shapiro  
Department of Chemistry  
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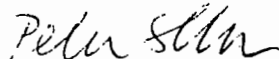
Re: Less sample - MORE signal. Change of address.

Dear Barry:

Thank you for the reminder. Please note the address change. The chemistry department at KTH will be equipped with a new AM-400 and an MSL-90. I will continue to use the FX-100 and XL-300 in Uppsala. We have successfully made FT-PGSE measurements on the XL, using a custom-built Varian 5mm switchable probe with integral anti-Helmholz gradient coils. The first results can be found in my review on FT-PGSE that will appear shortly in Progress in NMR Spectroscopy.

As a contribution I would like to comment on the prevalent opinion that more sample will always give a stronger NMR signal. Varian, in recent newsletters for example, recommend dilution of the sample (in the case of limited amounts of solute) to fill up the whole active sample volume on supercon systems. While this may usually be good practice, it is not a general rule. In a recent  $^{13}\text{C}$  study on 25% w/w Lithium dodecylsulphate micelles in water (P. Stilbs, O. Söderman and H. Walderhaug, J. Magn. Resonance, in press) we made the initially puzzling observation that the signal was far weaker than expected. The experiments were made on the FX-100 in the tuneable 10 mm multinuclear probe, using about 4 cm sample height in thin-wall 10 mm tubes. It was also observed that probe tuning was not behaving normally, requiring quite different settings as compared to a "normal" sample. Reducing sample volume to about 1.5 cm and adding a vortex plug removed all those problems. Sensitivity went UP by at least a factor of 5. Evidently the presence of a large volume of an electrically conductive aqueous solution in the probe did reduce its Q-value to a very significant extent. It is reasonable to assume that similar problems may arise in many studies on biological or biochemical samples, and one should consequently check for effects of sample volume. The effect on sensitivity could be very significant.

Yours Sincerely



/Peter Stilbs/



29 August 1986 (Received 8 September 1986)

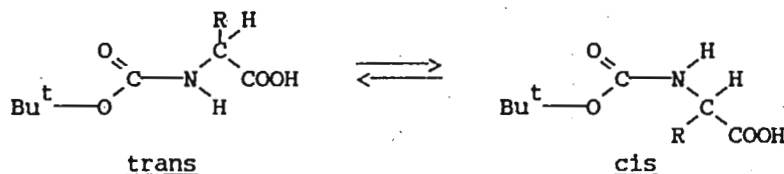
Professor B L Shapiro  
Department of Chemistry  
Texas A & M University  
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U S A

Amides Revisited: Cis/Trans Isomerism in Boc-Aminoacids

Roche Products Limited · PO Box 8 · Welwyn Garden City · Hertfordshire AL7 3AY  
Telephone Welwyn Garden 328128 Telex 262098 ROCHEW

Dear Barry

One of the consequences of introducing high field nmr spectrometers for organic chemists is the regular appearance in their spectra of unexpected and usually unwanted peaks, mostly due to solvent or other impurities, but occasionally to dynamic effects. For years we have been asked to run simple "Boc" and "Z" amino acid derivatives ( $\text{Boc-AA} = \text{Bu}^t\text{O.CO.NHCH(R)COOH}$ ,  $\text{Z-AA} = \text{PhCH}_2\text{O.CO.NHCH(R)COOH}$ ) at 100 MHz rarely seeing anything out of the ordinary. At 300 and 400 MHz we were therefore startled to see two unequal resonances for the NH proton in Boc-Glu ( $\text{R} = \text{CH}_2\text{CH}_2\text{COOH}$ ) in  $\text{d}_6$ -dmsO and in several mono- and diesters and amides. Under the fond illusion that monosubstituted amides existed entirely in the trans conformation in peptide derivatives, we started to hypothesise cyclic hydrogen bonded structures involving the glutamic acid  $\delta$  carbonyl. When checking other Boc- and Z-amino acids however, just about all of them showed two sets of peaks in  $\text{CDCl}_3$  or  $\text{dmsO-d}_6$ . A typical spectrum of Boc-Glycine in  $\text{dmsO-d}_6$  is shown in the Figure. Coalescence of the NH resonances at raised temperatures gave a  $\Delta G^\ddagger$  value of ca. 16 Kcals/mole. Therefore this phenomenon is certainly due to cis/trans isomerism about the amide bond in these urethanes.



We tentatively assign the major form in all cases as the cis form, based on the chemical shift of the amino acid  $\alpha$ -protons, which are probably at high field in the cis isomer, from previous work with thiocarbamate derivatives.<sup>1</sup>

Changing the amino acid hardly affects the cis/trans ratio, but changing the solvent does: e.g. in Boc-Glycine trans:cis :: 1:7.7 in  $\text{dmsO}$ , 1:1.5 in  $\text{CDCl}_3$ . Searching the Cambridge crystal data file, the majority of Boc-amino acids and peptides crystallise with the urethane amide bond



trans, but there are a few exceptions e.g. Boc-Phe, which are cis oriented. A literature search, which is what we should have done first, unearthed a paper describing this isomerism in Boc-Alanine and Boc-Ala peptides.<sup>2</sup> The reason why these dynamic effects were not obvious at 100 MHz is probably that the probes in electromagnets operate at least 15°C higher than in superconducting magnets.

We hope this contribution cancels out this years' pink ultimatum.

Yours sincerely

*Tom*

W A Thomas

*Ian*

I W A Whitcombe

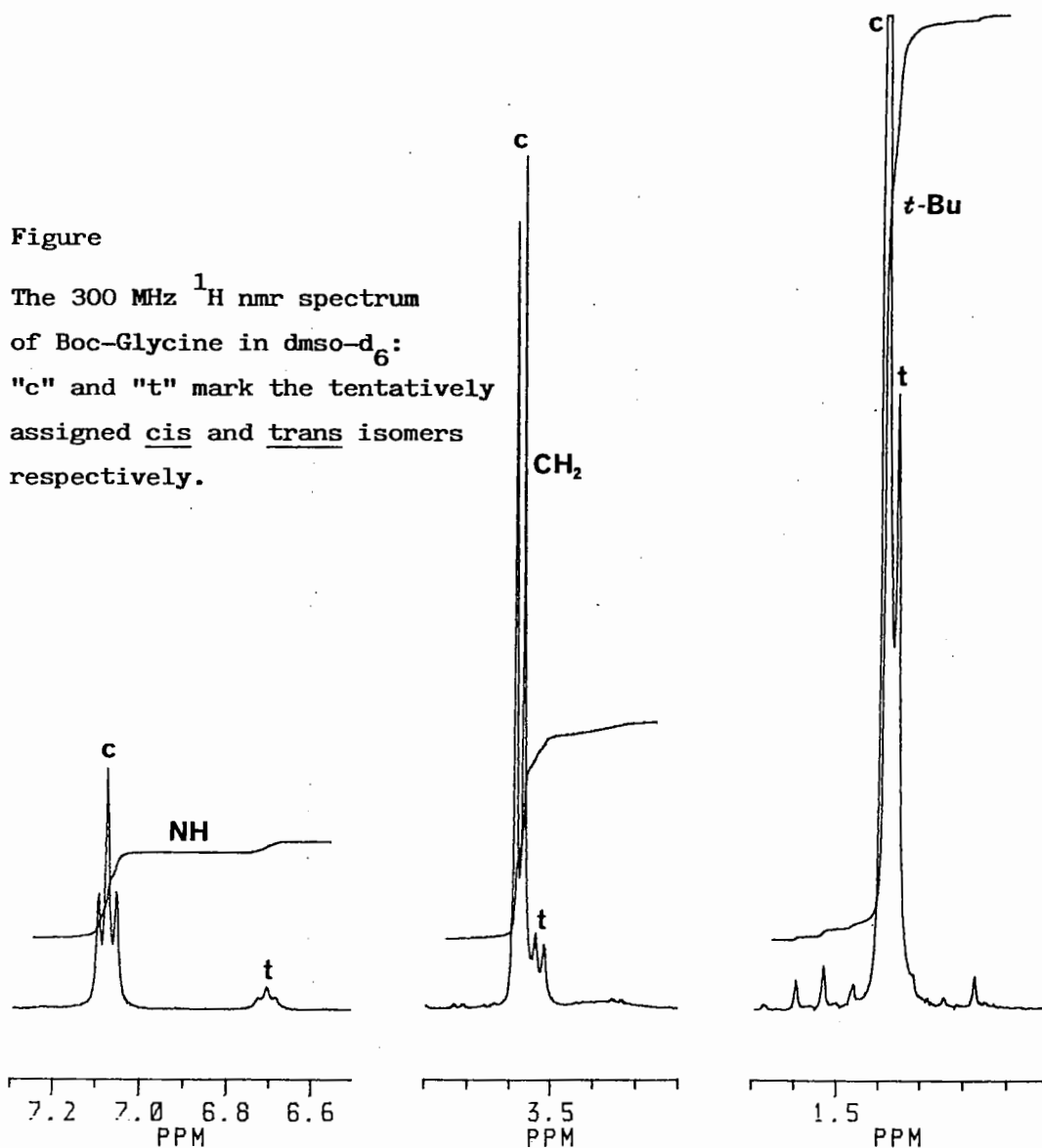
*Heather*

H S Simmonite

1. R A Bauman, J. Org. Chem., 1967, 32, 4129.
2. J. L. Dimicoli and M Ptak, Tetrahedron Letters, 1970, 2013.

Figure

The 300 MHz <sup>1</sup>H nmr spectrum of Boc-Glycine in dmsO-d<sub>6</sub>:  
"c" and "t" mark the tentatively assigned cis and trans isomers respectively.



Thomas L. James, Ph.D.  
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University of California, San Francisco ... A Health Science Campus

UCSF

September 1, 1986

(Received 8 September 1986)

Professor Bernard L. Shapiro  
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 College Station, Texas 77843-3255

### Tailored Excitation Using Fourier Transform Pairs: A Frequency-Space Notch Filter and One-Pulse Multislice Imaging Using Shaped Radiofrequency Pulses

Dear Barry:

FT NMR has employed only a few of the characteristics of FT pairs. The use of shaped rf pulses for selective excitation has been limited to: the gaussian pulse, whose fourier transform in the frequency domain is another gaussian<sup>1</sup>; the *sinc* function, whose fourier transform is a square wave<sup>1</sup>; and the *sech* function, whose fourier transform is another *sech* function<sup>3</sup>. The two former shapes have been used primarily for slice selection in NMR imaging, although their use for selective  $\pi/2$  pulses has been suggested<sup>1,2</sup>. And the latter shape has been shown to be a selective  $\pi$  pulse<sup>3</sup>. We have begun to explore a well-known relationship, known as the Modulation Theorem<sup>4</sup>, that exists between the two members of an FT pair,  $f(\nu)$  and  $F(t)$ :

$$\int [F(t) \times \cos(\omega t) \times e^{-2\pi i \nu t}] dt = (1/2)f(\nu - \omega/2\pi) + (1/2)f(\nu + \omega/2\pi).$$

We have chosen  $F(t)$  to be *sinc*( $t$ ), so that  $f(\nu)$ , the other member of the FT pair, is a square wave function. The resulting frequency-space function on the right side of the equation is two square waves separated by a frequency gap. In principle, it should be possible to position this gap to act as a square wave "frequency-space notch filter" in the excitation profile.

We have demonstrated that this theorem can be implemented on a 4.7 Tesla, 33 cm bore NMR system equipped with a Nalorac Quest 4300 Spectrometer, which incorporates a VAX 11/730 computer system and an array processor. Figure 1 illustrates the Modulation Theorem in the context of NMR imaging. Figure 1A shows a slice selected along the z-axis using a *sinc*-shaped pulse. Figures 1A through 1F show the effect of modulation by  $\cos(\omega t)$  when  $\omega$  is increased from  $\pi/3$  to  $2\pi$ . Note that the signal intensities in Figures 1B through 1F are each approximately 40% of the intensity of the slice in Figure 1A, which is close to the value of 50% predicted by theory. Figure 2 shows that when the frequency offset of the  $\cos(\pi t)$ -modulated *sinc* pulse is changed by  $\pm 4000$  Hz, both slices move in the same direction demonstrating that they are not quadrature images. This shows that it is possible to do multislice imaging in one pulse. Spectra with an excitation profile similar to that of the one-dimensional projections have also been obtained using a Hahn spin-echo technique. We have also used our "frequency space notch filter" for suppression of the water proton resonance and have shown that it is comparable to the 1331 pulse sequence for suppression of the water proton resonance, but it gives level excitation to the rest of the spectrum,

unlike the binomial series pulse sequences. The use of the FT pair that consists of the convolution of the *shah* function with *sinc(t)* has been used as a further extension of the one-pulse multislice imaging technique.

#### References:

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2. Sutherland RJ, Hutchinson JMS, *J Phys EB* 11, 217 (1978).
3. Silver MS, Joseph RI, Chen CN, Sank VJ, Hoult DI, *Nature* 310, 681 (1984).
4. Bracewell RN, "The Fourier Transform and Its Applications", 2nd Edition, McGraw Hill, New York, 1978.

Sincerely yours,

*Tom James*

T.L. James

*Ricardo Gonzalez-Mendez*

R. Gonzalez-Mendez

H.R. Engeseth

A.A.B. Gibson

J. de Olivares

L. Litt

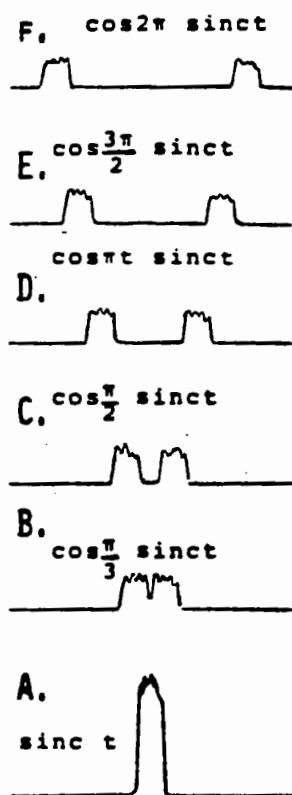


FIGURE 1.  
One-Dimensional  
z-axis magnetization

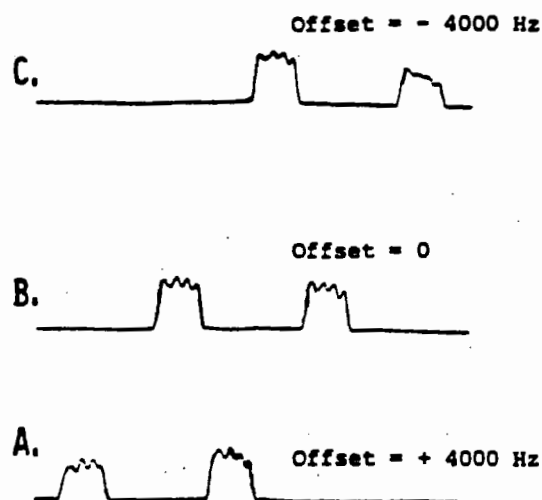


FIGURE 2. One-Dimensional z-axis  
magnetization when rf pulse shape  
is  $\cos \omega t \text{ sinc } t$

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Siegen, September 10, 1986  
(Received 19 September 1986)  
Tel. 0271/740-4390/4400

U.S.A.

COSY Experiments with Quadrupolar Nuclei:  $^7\text{Li}$  and  $^2\text{H}$

Dear Barry,  
our interest in COSY spectroscopy of quadrupolar nuclei continues. After completion of the  $^6\text{Li}$ ,  $^6\text{Li}$  experiment (THL 27, 2251 [1986]) we used the same cluster prepared with  $^7\text{Li}$ . As expected, the experiments proved to be more difficult because of faster Li relaxation ( $Q = -4.5 \times 10^{-2}$ , while for  $^6\text{Li}$   $Q = -8 \times 10^{-4}$ ). Therefore, a shorter  $t_1$  had to be used (Fig. 1).

$^2\text{H}$ ,  $^2\text{H}$  COSY is again less problematic and is the method of choice for the analysis of  $^2\text{H}$  spectra of perdeuterated compounds (Fig. 2). Needless to say that in both cases scalar coupling is not resolved in the 1D spectrum.

With kind regards,

Yours sincerely

*D. Moskau*

D. Moskau

*H. Günther*

H. Günther

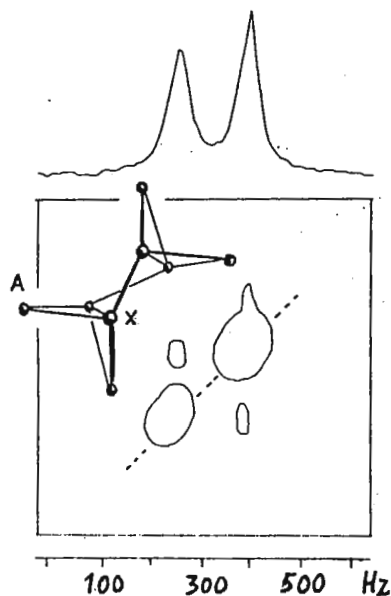


Fig. 1:  
COSY-45  
 $^7\text{Li}$ ,  $^7\text{Li}$   
spectrum;  
 $t_1(\text{max})$   
= 16 ms; 64  
increments  
of 0.25 ms

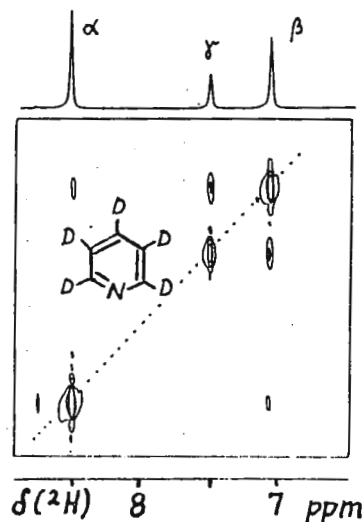


Fig. 2:  
COSY-45  
 $^2\text{H}$ ,  $^2\text{H}$   
spectrum  
of pyri-  
dine- $\text{D}_5$ ;  
 $t_1(\text{max})$   
= 0.213 s;  
0.4 s delay  
to empha-  
size small  
couplings



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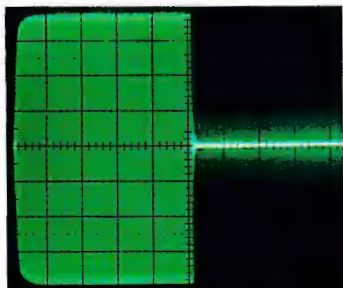
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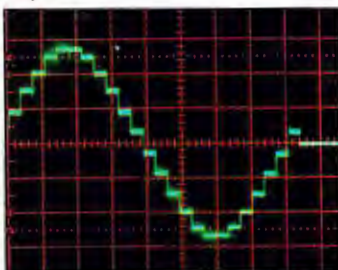
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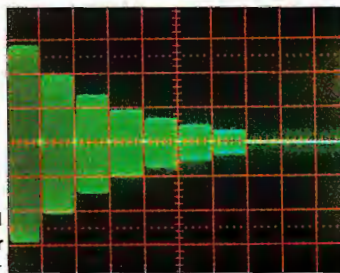
A  $5\mu\text{sec}$   $^1\text{H}$  observe pulse. ▽



$15^\circ$  phase shift through  $360^\circ$ . ▸



Shaped decoupler pulse. ▸



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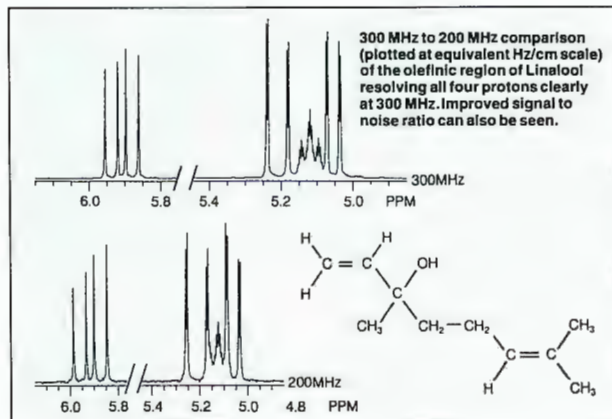
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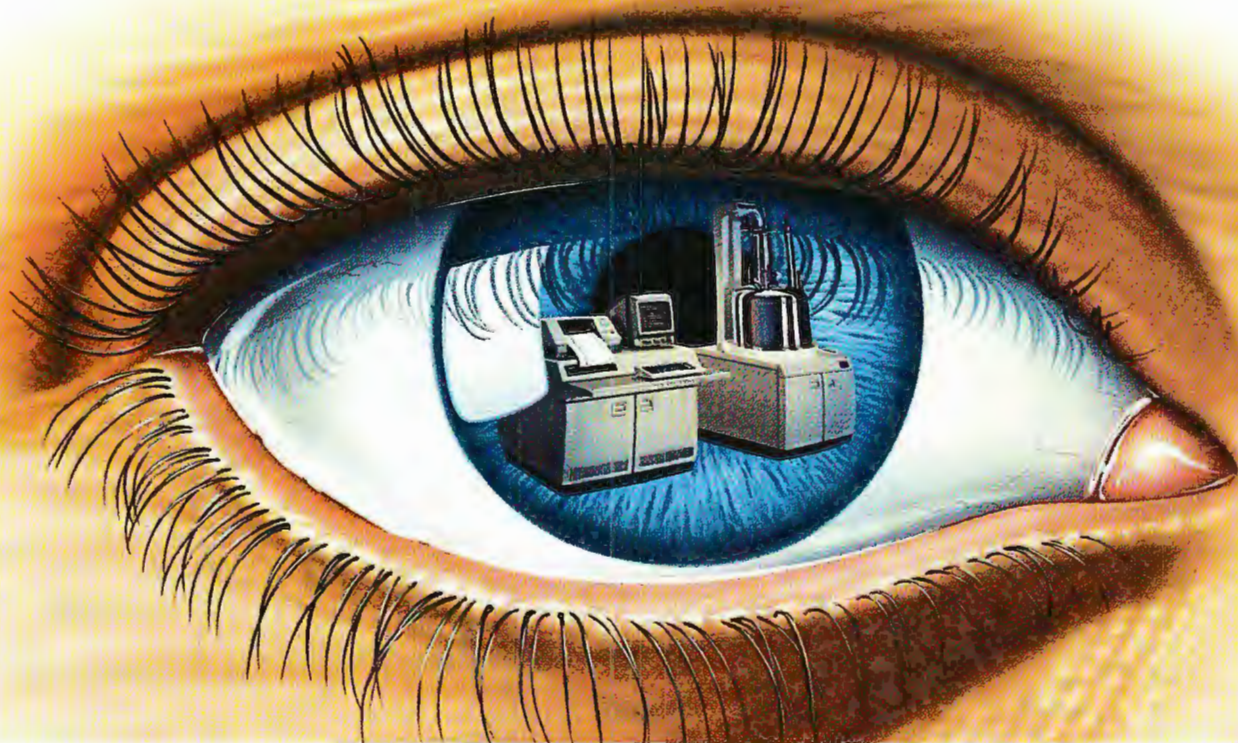
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Professor B.L. Shapiro  
Department of Chemistry  
Texas A&M University  
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U.S.A.

September 8, 1986

(Received 19 September 1986)

re: How to present 2D COSY spectra?

Dear Barry,

recently we had an argument with a referee who requested that the scales in a COSY spectrum should be given in ppm units. Since his view was supported by the editor we would like to solicit the opinion of others.

The argument held by the referee was essentially based on common experience and use of ppm units. We object the rule for two reasons: (i) if the axis presents broad-band decoupled spectrum (as  $f_2$  axis in heteronuclear COSY) with chemical shift information only, ppm units are preferable but, if the axis represents coupled spectrum, Hz units are at place, (ii) since the author is not always in a position to re-plot the spectrum any presentation rules should be made publicly known before being enforced.

Undoubtedly, the rate under which 2D spectra are published wears off as the method becomes more and more routine. This desirable trend will be accelerated by journal formal presentation rules. However, there will be always cases which will require presentation of a 2D spectrum. In such cases should be the axes in ppm or in Hz units? (Irrespective of IUPAC rules which call for Hz in diagrams).

Sincerely yours

  
Jan Schraml



# SYRACUSE UNIVERSITY

NMR and DATA PROCESSING LABORATORY  
GEORGE C. LEVY, DIRECTOR (315) 423-4026

DEPARTMENT OF CHEMISTRY, BOWNE HALL, SYRACUSE UNIVERSITY, SYRACUSE, N.Y. 13210

1 September 1986

(Received 9 September 1986)

Prof. Bernard L. Shapiro  
TAMU NMR Newsletter  
Department of Chemistry  
Texas A & M University  
College Station, TX 77843

Natural Abundance  $^{13}\text{C}$  NMR of Small  
Double-Stranded DNA Molecules

Dear Barry:

Natural abundance  $^{13}\text{C}$ -nmr of small double-stranded DNA molecules can provide detailed structural information, not readily available from other solution techniques.  $^{13}\text{C}$ -spectra of the nucleobases in DNA are sensitive to hydrogen bonding, especially for several of the carbons immediately bonded to heteroatoms acting as H-bond acceptors or donors. Thymine C4, guanine C2 and C6 are strongly deshielded (about 1 ppm) upon Watson-Crick base-pair formation, and cytosine C5, adenine C6, and the thymine methyl carbon are deshielded to a lesser extent. Shielding increases would be expected for these carbons due to ring current and steric effects in the absence of hydrogen bonding, so deshielding at these sites can be used to distinguish bases involved in Watson-Crick base pairs from unpaired bases. These conclusions are based on strand dissociation of three different DNA oligonucleotide duplexes. Figure 1 shows the bases and the hydrogen bonding sites and Fig. 2 gives  $\delta$  vs. T profiles for the guanine carbons in these duplexes; the negatively sloping profiles are for resonances which are most sensitive to H-bonding.

Netropsin binds to the central AT region of the octanucleotide duplex,  $[\text{d}(\text{G-G-T-A-T-A-C-C})]_2$ , and is thought to displace water specifically bound in the minor groove. In the netropsin:octanucleotide complex, +1.4 and -0.6 ppm changes in  $^{13}\text{C}$  chemical shift are noted for one thymine C2 and one adenine C4 resonance, which are atomic neighbors of putative hydrogen bonding sites for water or netropsin. These and other observations provide direct support for the existence in solution of a "spine of hydration" in  $^{13}\text{C}$  segments of DNA that is displaced upon netropsin binding.  $^{13}\text{C}$  chemical shifts show promise as a method for the determination of hydrogen-bonded sites in complexes of nucleic acids with themselves and other ligands.

Sincerely,

Philip N. Borer  
Research Associate Professor  
and Associate Director

*P N Borer*

George C. Levy  
Professor  
and Director

*George C. Levy*



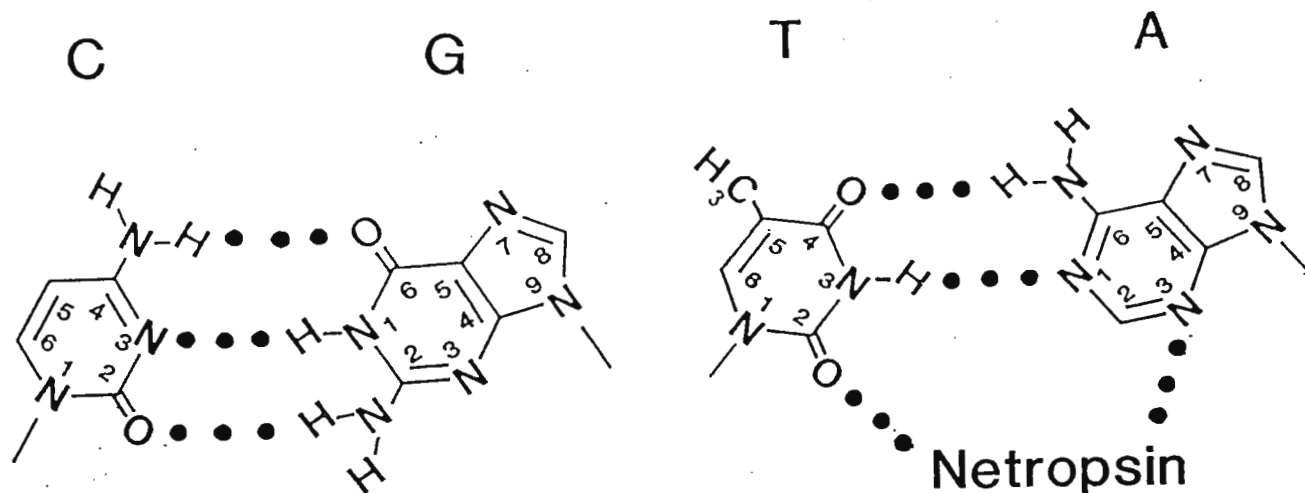


Figure 1. Base pairing schemes in (a) Cyt-Guo and (b) Thd-Ado, netropsin and water hydrogen bond to ThdO2 and AdoN3.

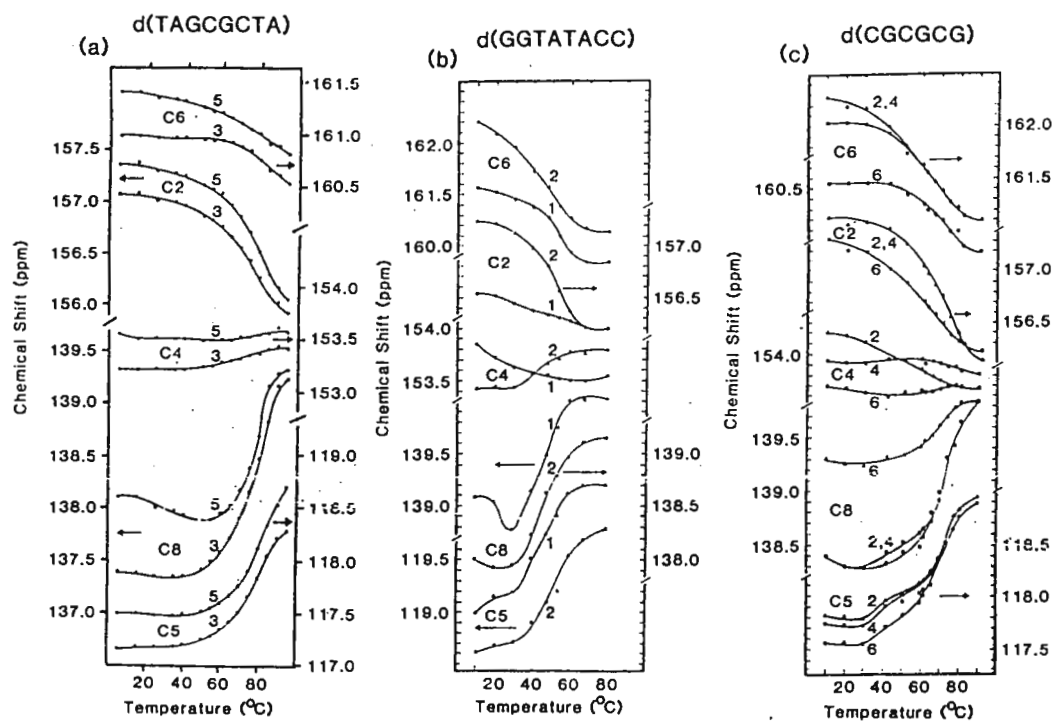


Figure 2. Chemical shift vs. temperature profiles for the guanine carbons of three oligonucleotide duplexes; shielding increases toward the bottom of each panel.



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September 5, 1986

(Received 16 September 1986)

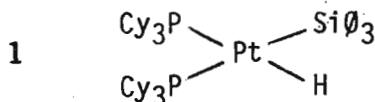
BITNET  
TS6191 at OSH TVMAPlatinum hydride lineshape  
analysis; BITNET;  
NSF Budget in JeopardyProfessor B. L. Shapiro  
Department of Chemistry  
College Station, TX 77843

Dear Barry,

In response to the pink note, here are some recent results and general remarks.

**Platinum hydride NMR**

From time to time molecules are found where dynamic effects allow determination of relative signs of coupling constants. Such is the case for the hydride resonance of several diphosphinosilylplatinum hydrides, eg. 1. We have been analyzing the hydride lineshapes in collaboration with Mark Hampton-Smith and H. C. Clark at Guelph.

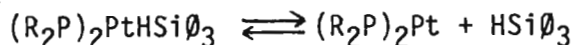


$\phi$  = phenyl  
Cy = cyclohexyl

Hydride is coupled to both phosphoruses as well as  $^{195}\text{Pt}$ . So the hydride spectrum (toluene- $\text{D}_8$  solution) consists of one quartet for 1 with non-magnetic platinum flanked by the two quartets coming from 1- $^{195}\text{Pt}$ . The effect of intramolecular exchange of silicon for hydride is to average the cis and trans hydride phosphorus couplings. At slow exchange rates this has the effect of broadening the outside lines of each quartet whereas the inside lines always remain sharp.

One such unaffected transition is  $\alpha\alpha\alpha \longleftrightarrow \alpha\alpha\beta$  the order of spins being  $p^1$ ,  $p^2$  and H. From the density matrix equations one can see that the separation between the inside lines is  $J_{\text{cis}} + J_{\text{trans}}$  (both P, H couplings) whereas the gap between the two outside broadened lines is  $J_{\text{trans}} - J_{\text{cis}}$ , hence these two  $^{31}\text{P}$ ,  $^1\text{H}$  coupling constants must have opposite signs.

Above  $25^\circ$  all hydride resonances broaden as a result of fast reversible dissociation. We have incorporated both exchange processes into the density



matrix equations using our PI method and hence fished<sup>1</sup> out activation parameters for both processes<sup>2</sup>, to be duly published.

#### NMRNET

Now a word about communications: To facilitate interaction among Newsletter people I propose that all your contributors who have BITNET addresses include them on future contribution to the Newsletter, as I have. BITNET is an electronic mail system which interconnects many universities and research institutes throughout the free world. TAMUNMR could then put together a directory of BITNET addresses. The obvious advantages of BITNET is speed and it's free. One can send a manuscript (without the figures) half way round the world in a minute.

Further information on BITNET is available at your local computer center.

#### NSF Budget in Jeopardy

Readers may be aware that the NSF budget which so far sailed through Congress without a scratch has just suffered a serious cut of \$145.7M at the hands of the House Appropriations Subcommittee on HUD Independent Agencies. This puts the NSF budget \$145.7M below the Administration's request. One can only hope that the Senate Appropriations Subcommittee on HUD-Independent Agencies will put some or all of this back, then, that the Conference Committee will at least agree to the original request. Hopes are more likely to be realized if lots of scientists write to Jack Garn, Chairman of the above Senate Subcommittee and explain why the NSF needs the money, what will happen to their programs if the NSF budget is cut, what sort of future the country will have with defunct science.

Directly or otherwise NSF funding is critical to all Newsletter writers. A one \$trillion budget is currently being carved up. Whether or not there will be something left in it for us depends on how active scientists are politically, what we say to Congressmen. If we don't speak up now we shall only have ourselves to blame when the funding we hoped would be for science goes somewhere else.

Senator Garn's address is US Senate, Washington, D.C. 20510, Tel. #202-224-5444, subcommittee at 202-224-3471.

Best wishes.



Gideon F. Fraenkel  
Professor of Chemistry  
Is

Yours sincerely,



Albert Chow  
Research Associate

1. J. I. Kaplan and G. Fraenkel, NMR of Chemically Exchanging Systems, Academic Press, New York, 1980, Chap. 6.
2. A. Chow, A. C. Clark, G. Fraenkel, D. H. Grossie, M. J. Hampton-Smith, D. F. Mullica and R. Ruegger, to be published.



## DEPARTMENT OF HEALTH &amp; HUMAN SERVICES

Public Health Service

National Institutes of Health  
Bethesda, Maryland 20892  
Building : 30  
Room : 106  
(301) 496- 5750

September 4, 1986 (Received 8 September 1986)

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

Dear Professor Shapiro:

"Free Running" of Nicolet  
Explorer Interface

We've had an intermittent problem with the interface between our Nicolet 2090 Explorer scope and 1280 computer for the past 18 months. When first installed, the scope would occasionally start to transfer data repeatedly (cycle time less than 50 ms), regardless of the delay time setting, without accumulating signals. Recently we've been able to make the system fail consistently, enabling us to locate the source of the problem.

The problem was caused by a glitch picked up on the 'Record' line. When the 1280 told the 2090 to arm itself for the next trigger, the 'ARM' pulse caused a glitch on the 'RECORD' line high enough to propagate through IC20 and IC19, by which time it was a clean 100 ns pulse resetting IC4. This caused a 'POST RECORD' signal to appear, telling the Computer and Explorer to transfer data again, and again.... The problem was solved by connecting a .03 $\mu$ F capacitor from IC20 pin 1 to IC20 pin 7 (GND) to suppress any glitch.

Sincerely yours,

Rolf Tschudin  
Laboratory of Chemical Physics  
NIADDK

Yukio Hiyama  
Bone Research Branch  
NIIDR

Please credit this to  
Dennis Torchia's account



# Automation makes it easy to use... Standard "extras" make it easier on the budget

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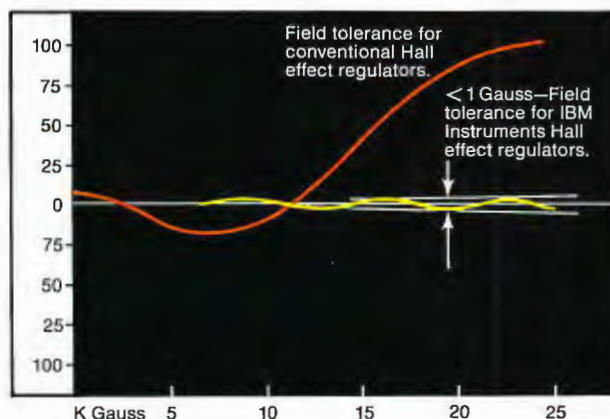
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 INORGANIC CHEMISTRY: PROFESSOR B. O. WEST  
 ORGANIC CHEMISTRY: PROFESSOR W. R. JACKSON

Wednesday 10 September, 1986

(Received 16 September 1986)

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

## Spin-Spin Coupling Mechanisms

Dear Barry

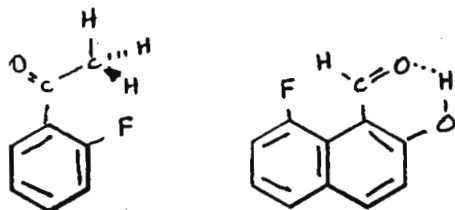
Since we 'met' in the lonely hearts section of TAMU NMR Newsletter in 1982, Professor Ruben Contreras and I have been collaborating on an investigation of mechanisms by which spin-spin couplings are transmitted. Theoretical work is done in Buenos Aires, molecular design is a shared activity, synthesis and spectroscopy done here in Melbourne. Initially our progress was slow but we are now making good progress and enjoying by mail some Southern Hemisphere cameraderie.

The IPPP method used by the Contreras group predicts that coupling between carbon and a heteroatom X is enhanced when a C-H bond occupies the space between C and X. Our first success (1) was in finding a predicted  $^3J_{CF}$  of 3 Hz in o-fluoroacetophenone and also a  $^4J_{CF}$  to the methyl group of the predicted 7 Hz, which had been overlooked by earlier workers.

The C-H bond in this case is not in the main plane of the molecule and the calculations suggested a large increase in J if coplanarity could be achieved. It is, too - in the 8-fluoronaphthaldehyde shown below, for which  $^4J_{CF}$  is 26.2 Hz. This is not the calculated value (77 Hz) but then our molecule probably does not have the simple geometry shown and the calculated values are extremely sensitive to the hydrogen-fluorine separation. We await the crystal structure.

We hope that we can synthesize naphthalenes of this kind with other heteroatoms in place of fluorine, so further tests of theory are in store.

I'm sorry to conclude this letter with the news that Stan Johns, who worked at a nearby CSIRO laboratory and shared David Kelly's TAMU subscription, died last month after a long struggle with multiple myeloma. He'll be missed.



Kind regards

*Ian*

Ian D. Rae

1. Contreras, Giribet, Natiello, Perez, Rae and Weigold, Aust. J. Chem., 1985, 38, 1779-1784.

# Raychem

Raychem Corporation  
300 Constitution Drive  
Menlo Park, California 94025

Telephone 415) 361 3333  
TWX 910 373 1728  
Telex 34 8316

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

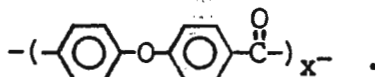
September 10, 1986

(Received 23 September 1986)

## Solid-State NMR Characterization of Poly(aryletherketone)'s

Dear Professor Shapiro:

We are interested in using solid-state NMR to characterize the effects of processing on poly(aryletherketone)'s. These materials enjoy good mechanical properties in conjunction with high thermal and chemical stability, which make them attractive for many specialty plastics applications. To date, we have concentrated on PEK, represented by



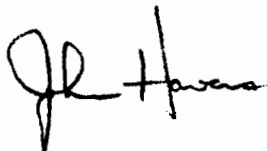
The degree of crystallinity, the orientation of crystalline and noncrystalline chains, and the presence of any low molecular weight species remaining after the workup constitute our current focus.

The accompanying table presents  $^1\text{H}$  spin-lattice relaxation times in both laboratory and rotating frames for PEK subjected to different processing histories. All samples were sealed under nitrogen in glass tubes. The  $^1\text{H}$   $T_1$ 's (at 180 MHz) are sufficiently long to permit spin diffusion measurements as a means of characterizing the morphology in the tens of nanometers regime. They also indicate a considerable difference among the samples in relaxation efficiency.

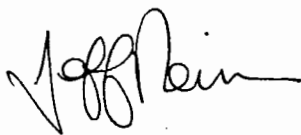
The  $^1\text{H}$   $T_{1\rho}$  decays have been decomposed into sums of exponentials by nonlinear least squares fits. The short component ( $< 5$  msec) is probably due to mobile noncrystalline material; the intermediate component (10-20 msec) to crystalline regions; and the long component ( $\geq 100$  msec) to residual bound water. This last assignment is made by observing the proton lineshape following various periods of spin locking. The long  $T_{1\rho}$  component has a relatively narrow lineshape, which suggests a mobile, proton-bearing species. Attempts to assign the chemical shift of this component by using magic-angle spinning to average the remaining dipolar coupling and chemical shift anisotropy have not yet been successful because of a residual proton signal in the spinning probe. If the assignment of the slowly relaxing component to residual water is correct, extended drying of the material well above its glass transition temperature (165°C) does not completely remove adsorbed water from the polymer. Efforts to improve the accuracy of the quantitative results by using multiple-pulse relaxation are currently underway.

# Raychem

This work was performed in Jeff Reimer's laboratory at the Chemical Engineering Department of U.C. Berkeley.



John Havens  
Raychem Corporation



Jeff Reimer  
U.C. Berkeley



Karl Amundson  
U.C. Berkeley

## Spin-Lattice Relaxation Results for PEK

SAMPLE	$T_1$ (sec)	SPIN-LOCK $T_{1\rho}$ AT 5.1 GAUSS	
Amorphous sheet before annealing	1.3	2.8 msec 130 msec	99.7% 0.3%
Amorphous sheet after annealing for 6 hours at 250°C	2.0	3.7 msec 18 msec	73% 27%
Powder	4.7	2.8 msec 11 msec 100 msec	62% 36% 2%
Spun fiber (5.2 x melt draw) oriented $\perp \vec{B}_0$	13	2.6 msec 13 msec 240 msec	85% 15% 0.3%



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69622 VILLEURBANNE Cedex

Tél. 78 89 81 24 (secrétariat poste 33.70 ou 32.10)

Villeurbanne, le 12 Septembre 1986

(Received 24 September 1986)

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

Titre : MODIFICATION DE LA SEQUENCE D'ECHOS STIMULES ET MOUVEMENTS  
LIQUIDIENS

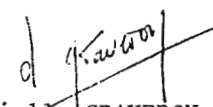
Cher Professeur Shapiro,

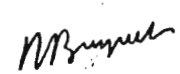
L'emploi des échos stimulés en imagerie RMN prend de plus en plus d'importance car cette technique s'applique à de nombreuses situations : imagerie avec pondération par le temps de relaxation spin-milieu, imagerie multicoupe, imagerie spectroscopique, imagerie rapide et imagerie de débits (1). Les échos stimulés s'utilisent également pour la localisation spatiale des observations spectroscopiques (2).

En présence de mouvements liquidiens on peut tirer profit des échos stimulés, à condition d'introduire une modification de la séquence de base. En effet si une impulsion de  $180^\circ$  est placée au milieu de l'intervalle de temps  $t_2$  séparant la seconde et la troisième impulsion de  $90^\circ$  (Figure 1), la refocalisation des aimantations transversales observée habituellement à  $t_3 = t_2$  et  $t_3 = t_2 \pm t_1$  ( $t_2 > t_1$ ) a lieu à la date de l'écho stimulé ( $t_3 = t_1$ ). Ce dernier est dû aux aimantations longitudinales qui sont "gelées" le long de l'axe Oz pendant l'intervalle  $t_2$ . Le choix de la phase de l'impulsion de  $180^\circ$  permet soit l'addition, soit la soustraction des échos transverses et longitudinaux pour  $t_3 = t_1$ . Si, pendant  $t_2$ , un gradient bipolaire est appliqué dans la direction d'un écoulement, l'intensité de l'écho global est alors modifiée en raison du déphasage  $\phi = \gamma G_y v \tau (\tau + \tau')$  acquis par l'aimantation transversale. Dans tous les cas cette intensité tend, lorsque  $\phi$  est élevé, vers une valeur limite  $I_0$ , indépendante de la vitesse  $v$ . Lorsque les échos transversal et longitudinal sont opposés, les signaux en provenance d'éléments fixes de l'échantillon ont donc une intensité plus faible que  $I_0$ . On modifie ainsi le contraste d'une image en faveur des éléments en mouvement. Une illustration est donnée sur la Figure 2.

Un des intérêts de cette méthode est qu'elle permet d'incorporer avec souplesse les différentes étapes de préparation du signal (codage de phase, conversion vitesse/phase puis phase/amplitude) dans une séquence relativement simple. Une autre utilisation de cette séquence d'échos stimulés modifiée, peut s'envisager pour l'étude de la diffusion.

Recevez, cher Professeur Shapiro, nos meilleures salutations.

  
Danielle GRAVERON

  
André BRIGUET

  
Hana LAHRECH

(Contribution à mettre au crédit du Laboratoire de Résonance Magnétique Nucléaire - Professeur Jean DELMAU)

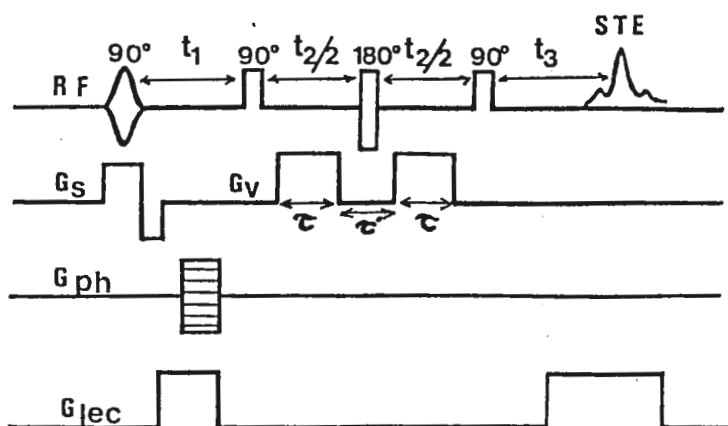


Figure 1 : Séquence d'écho stimulé modifiée par une impulsion de  $180^\circ$  placée au milieu de l'intervalle de temps  $t_2$ .  $G$  = gradient de sélection  
 $G_v$  = gradient de codage de la vitesse  $G_{ph} \equiv$  gradient de codage de phase  
 $G_{lec}^v$  = gradient de lecture

(Cas d'une image pondérée par les vitesses perpendiculaires au plan de coupe)

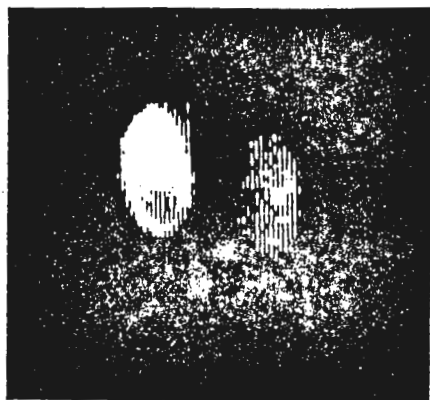
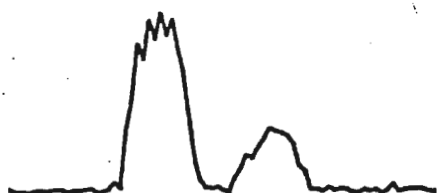


Figure 2 : Contraste observé entre deux tubes (1,2 cm diamètre) contenant de l'eau en mouvement (3 cm/s, à gauche) et immobile (à droite). Le profil correspondant est également donné au dessus de l'image.

#### Références :

- (1) D. MATTHAEI et al, Magn. Res. Med. 3, 554 (1986) et références citées
- (2) G. Mc KINNON, 5th Meeting SMRM Montréal (Aug. 86)
- (3) J. FRAHM et al, 5th Meeting SMRM Montréal (Aug. 86)

villanova  
university

VILLANOVA, PENNSYLVANIA 19085

Department of Chemistry

Direct Dial Number: (215) 645-4840

August 27, 1986

(Received 1 September 1986)

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

Dear Professor Shapiro:

HETCOR of NORTRICYCLYL BROMIDE.

We have recently been interested in using the  $^1\text{H}$  and  $^{13}\text{C}$  spectra of nortricycyl bromide (A) to assist in the interpretation of the complex spectra of isomer mixtures from the reaction of the new halonium transfer reagents with bicycloalkenes. A literature search has revealed little information on the spectral assignments for A.

It is fairly easy to assign H3, H4, H7syn, C3 and C4 in the 1D-NMR spectra, while DEPT indicates which carbon resonances are methylenes. In addition, the 18.2 ppm resonance can be assigned to C2 since it is 8.3 ppm downfield from the parent hydrocarbon shift. Further assignments from the 1D-NMR spectra are difficult, especially for the  $^1\text{H}$  1.0-1.5 ppm region.

Heteronuclear correlation (HETCOR) 2D-NMR has proven valuable for completing the assignments, especially for unravelling the crowded proton region. Figure 1 shows a HETCOR run on a Varian XL-200. The 31.0 ppm resonance correlates with two well separated  $^1\text{H}$  resonances where the H7syn resonance is shifted 1.3 ppm downfield from H7anti due to the effect of the 3-exo-bromine. The C5 resonance correlates with the H5 methylene protons which are expected to give a narrow proton pattern with a shift similar to H7anti. H1 is expected to be shifted downfield from H6 since it is closer to the bromine. On the other hand, the bromine causes greater steric compression on C1 than on C6. It is expected that the C1 resonance will come upfield of the C6 resonance. Figure 1 nicely demonstrates this correlation. We are presently attempting to confirm this last point by means of a carbon-carbon connectivity experiment.

Please credit this to the account of Dr. Amos J. Leffler.

Sincerely,



Walter J. Boyko, Ph.D.  
NMR Laboratory Directory

(continued on page 33)

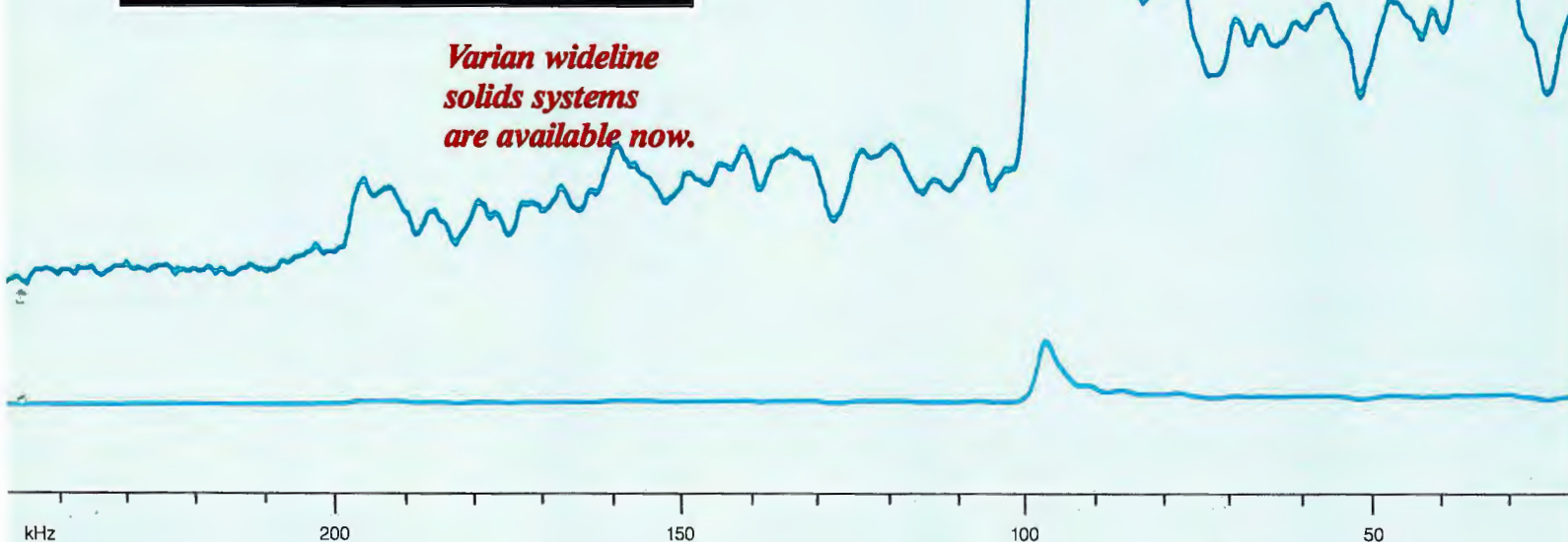
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$^{23}\text{Na}$  NMR powder spectrum of  $\text{NaNO}_3$  showing detailed crystallite distribution within the sample.



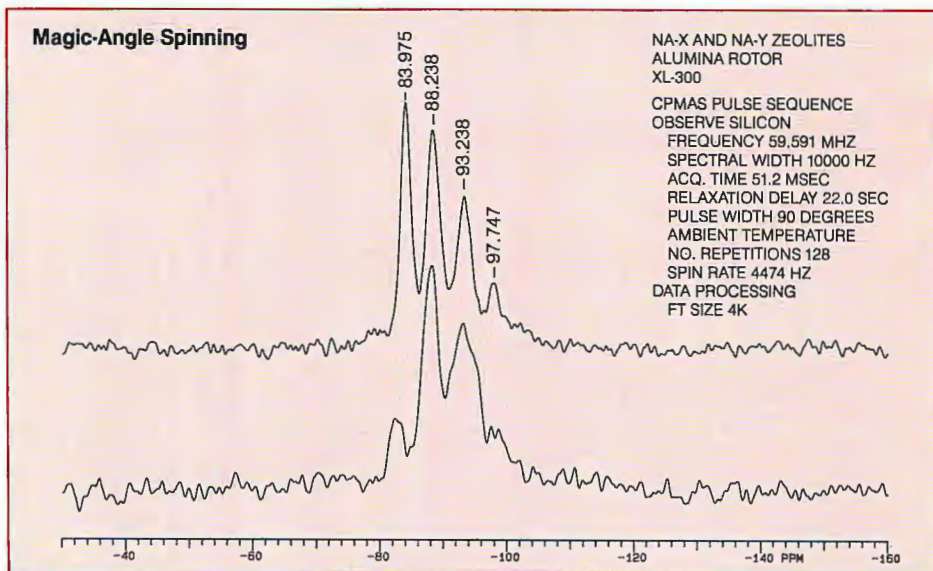
# Solid-State Results from Varian NMR

## <sup>29</sup>Si MAS - Zeolites

Silicon is the major nucleus of interest in silicates. MAS reveals information about the types of Si present in a sample. The upper spectrum is of Na-X, which has a lower Si/Al ratio than does Na-Y (lower spectrum).

The resonances correspond to Si[4Al] (lowfield) through to Si[0Al] (highfield). Neither of these Si spectra have been run with cross-polarization, as there are few, if any, framework protons present. However, CP/MAS experiments are used when investigating adsorption of small molecules onto zeolites.

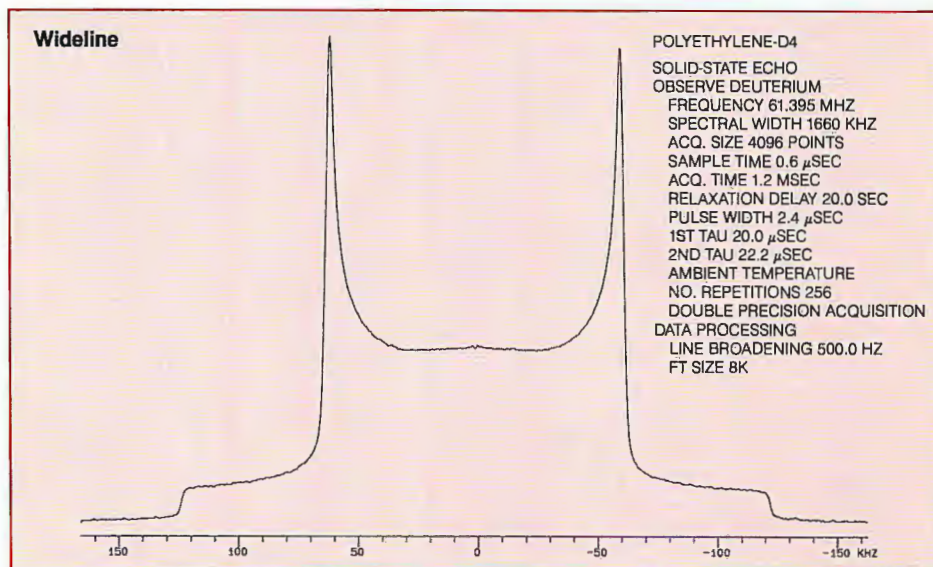
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## Poly (ethylene-d<sub>4</sub>)

The sample shown here was mainly crystalline (which gives the doublet spectrum), with some amorphous material (showing as a central hump). The crystalline T<sub>1</sub> relaxation is long, demanding a 10-second wait between acquisitions. Techniques such as this have been used to investigate the chain orientations of stressed or drawn samples. Molecular order may be correlated to sample morphology using spectra such as this.

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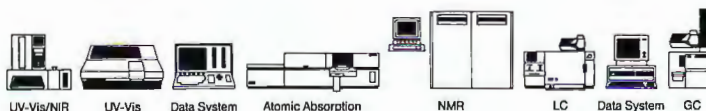
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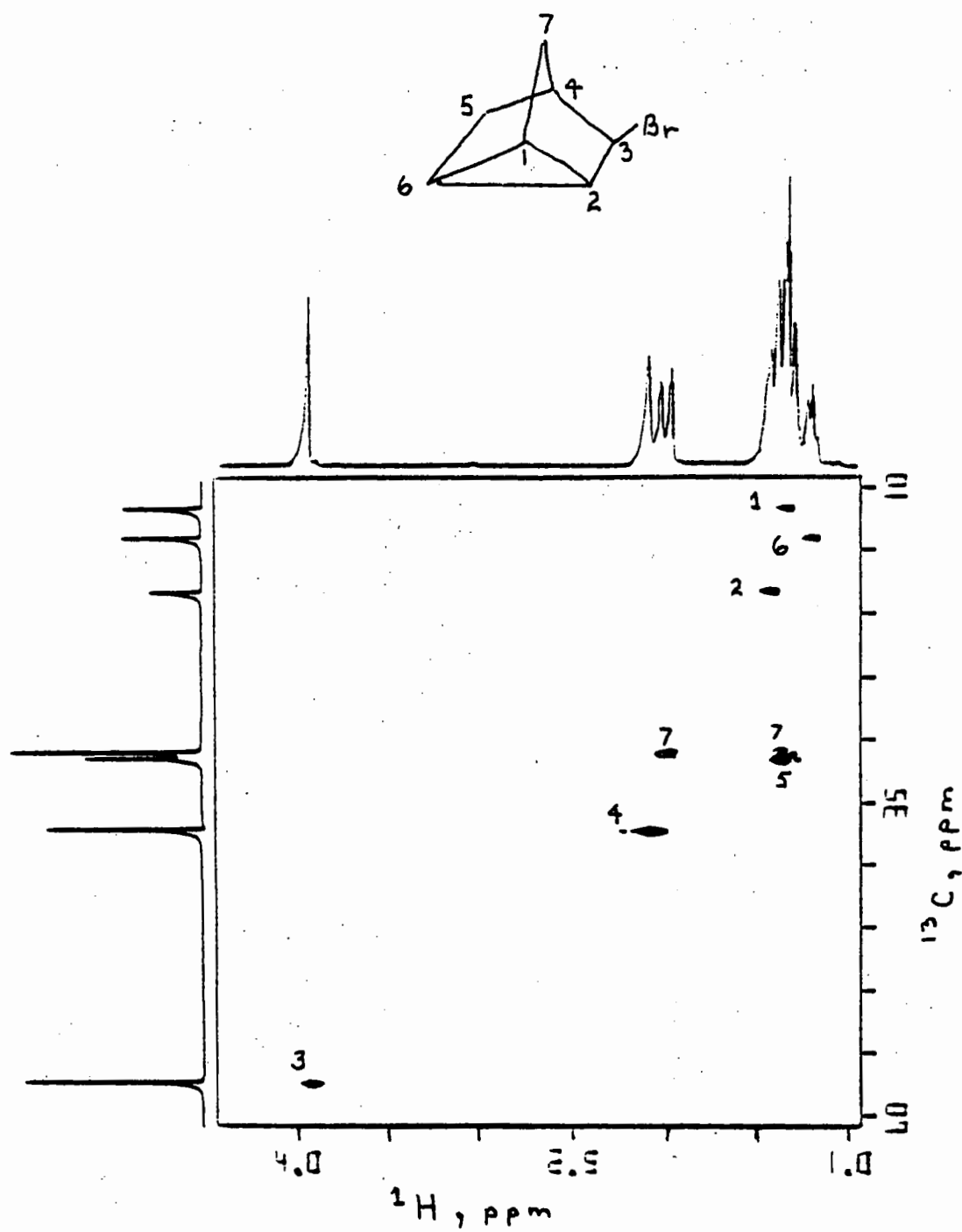


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(continued from page 30)

Figure 1







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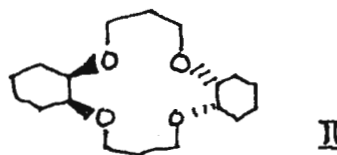
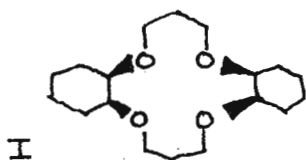
17 September, 1986  
(Received 24 September 1986)

Professor B.L. Shapiro, Editor  
TAMU NMR Newsletter  
Dept. of Chemistry  
Texas A & M University  
College Station, Texas  
77843-3255  
U.S.A.

Dear Professor Shapiro,

Title: "Stereochemical Dynamics of a Dicyclohexano-14-C- 4"

Recently, Bob Kirby, as part of his B.Sc. Honours Project and now M.Sc. research, has purified one configurational isomer from the catalytic hydrogenation of dibenzo-14-C-4. As yet we do not know if it is cis-syn-cis I, or cis-anti-cis II, but it does have a most interesting 100 MHz  $^{13}\text{C}$  NMR behaviour as a function of temperature.



From a simple 5 line spectrum at 298K in  $\text{CD}_2\text{Cl}_2$  solvent, the spectrum at 183 K becomes that shown on the subsequent page.<sup>2</sup> There are two temperature dependent phenomena occurring it appears. The first is degenerate cyclohexane ring inversion and the second is non-degenerate ring inversion of the 14-membered macrocycle.

For 14-C-4 itself<sup>(1)</sup>, no coalescence phenomena have been observed, albeit at 15 MHz, in the  $^{13}\text{C}$  spectra down to 143K. These authors<sup>(1)</sup> did suggest, however, based on chemical shift changes in  $\text{CHCl}_2\text{F}$  solution, that at least two conformations of 14-C-4 were present.

We are in the process of isolating the second configurational isomer from the hydrogenation product and are using high field spectra to study it as well as 14-C-4. Hopefully our crystals of I and II will be of sufficiently good quality for X-ray analysis.

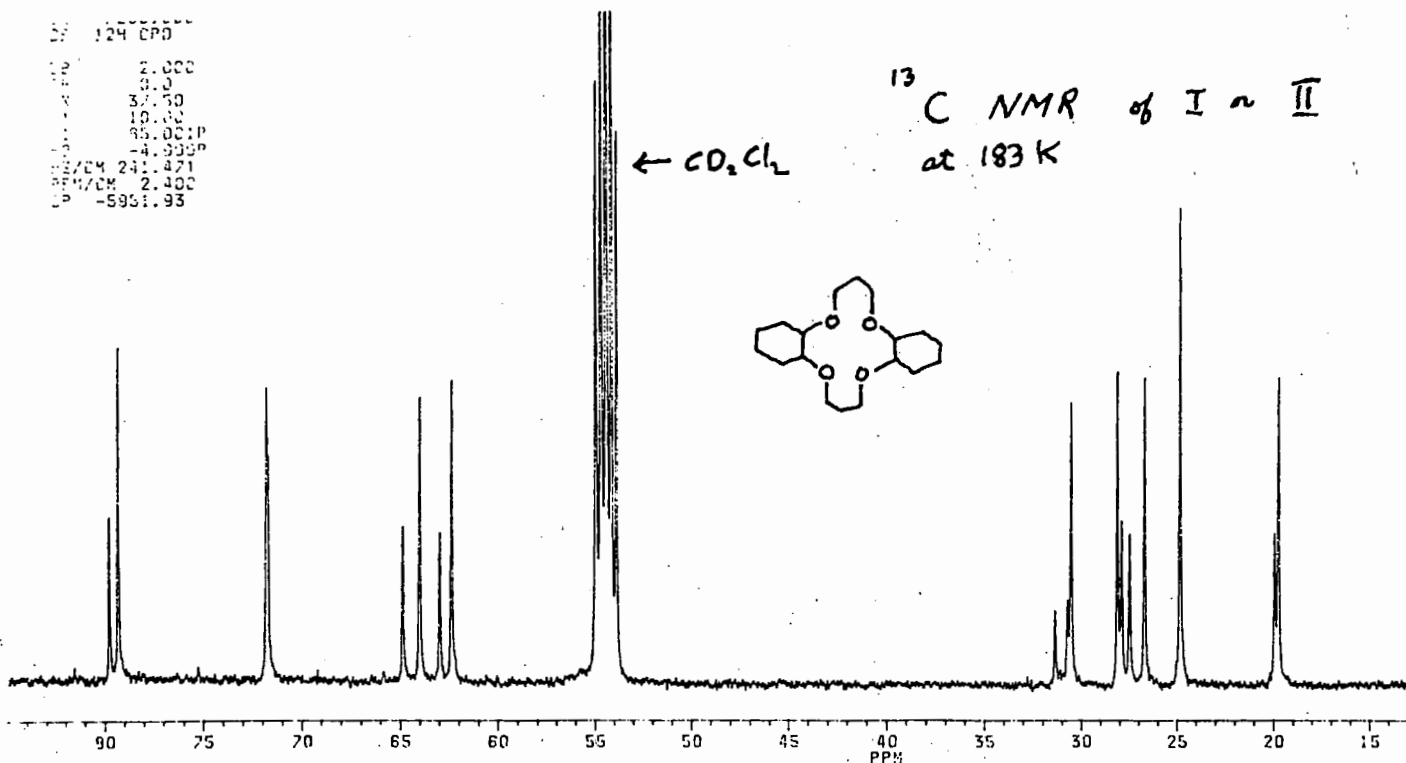
Sincerely,


G.W. Buchanan,  
Professor of Chemistry

GWB/cm

Ref. (1) G. Borgen, J. Dale and G. Teien. Acta. Chem. Scand. B(33) 15-21 (1979).

P.S. I'd like to thank Bob Fleming at the Univ. of Nottingham for the spectrum shown here, obtained during my recent mini-sabbatical in the U.K.



## IN SEARCH OF

The Chemistry Department at the University of Wyoming is searching for either a room or variable temperature  $^1\text{H}$  probe for a Varian EM-360. If you have a probe (or instrument) available for purchase, please contact either Dr. Ed Clennan, Chemistry Department, University of Wyoming, P.O. Box 3838, University Station, Laramie, Wyoming 82071 (Tel. 307-766-6667) or Dr. Daniel A. Netzel, Western Research Institute, P.O. Box 3395, University Station, Laramie, Wyoming 82071 (Tel. 307-721-2370).



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EN NATUURWETENSCHAPPEN  
KATHOLIEKE UNIVERSITEIT  
NIJMEGEN, NEDERLAND

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

Uw kenmerk

Uw brief van

Ons kenmerk  
U10158/WV/DvdW

Datum

September 12, 1986

Onderwerp

(Received 22 September 1986)

Dear Professor Shapiro,

## HIGH TEMPERATURE $^{23}\text{Na}$ NMR OF ZEOLITE NaA

In recent years there has been considerable interest in the NMR of zeolites. Several nuclei in zeolites can be studied,  $^{29}\text{Si}$ ,  $^{27}\text{Al}$ ,  $^1\text{H}$ ,  $^{23}\text{Na}$  to mention a few. Especially magic angle spinning has proven to be very valuable to increase the spectral resolution, in particular for  $^{29}\text{Si}$ . Although MAS can be applied with success as well to quadrupolar nuclei like  $^{27}\text{Al}$  and  $^{23}\text{Na}$ , the gain in resolution for these nuclei is not so great as for spin  $-\frac{1}{2}$  nuclei. The quadrupole interaction for half-integer spins very often gives characteristic spectra even in the absence of magic angle spinning. Also two-dimensional nutation NMR (1,2) can help to increase the resolution.

Without the experimental restrictions imposed by magic angle spinning, it is not difficult to construct a probe for high temperatures. Fig. 1 shows  $^{23}\text{Na}$  NMR spectra of zeolite A obtained with such a high-temperature probe as a function of temperature. To explain these spectra, Fig. 2 shows roomtemperature  $^{23}\text{Na}$  spectra of zeolite A, dried at  $300^\circ\text{C}$  for 48 hours at  $10^{-2}$  Torr at a 300 (CXP 300) and 500 (AM 500) MHz spectrometer. Clearly, at least two different sites are observed, one with a large quadrupole interaction giving a field dependent splitting, the other with a rather small splitting. By increasing the temperature to  $680^\circ\text{C}$ , so far the highest temperature obtained, first the lines corresponding to the broad second-order quadrupole pattern disappear and then the quadrupole line at the center narrows. No doubt the increased motion of the sodium atom at higher temperatures is responsible for this narrowing. A detailed discussion will be presented elsewhere, but the result shows that NMR of zeolites at temperatures where they are used as catalysts, is worthwhile. In the first prototype of the probe with which these spectra are taken, the sample was placed in an oven heated by a DC current. This causes small shifts and therefore in the new design the sample is heated by nitrogen gas, heated outside the probe. The signal denoted by a star is due to a folded-over Cu signal.

Best regards,

Ron Janssen

Ery Tijink

Wiebren Veeman

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(2) A.P.M. Kentgens, J.J.M. Lemmens, F.M.M. Geurts and W.S. Veeman, in press, J. Magn. Res.



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NIJMEGEN

# LABORATORIUM VOOR FYSISCH CHEMIE

Toernooiveld, Nijmegen  
Telefoon (080) 55 88 33

Geadresseerde  
Professor B.L. Shapiro

Ons kenmerk  
U10158/WV/DvdW

Datum  
12-9-'86

Blad No  
-2-

Fig. 1: Temperature dependent  
 $^{23}\text{Na}$ -NMR spectra of  
zeolite A.

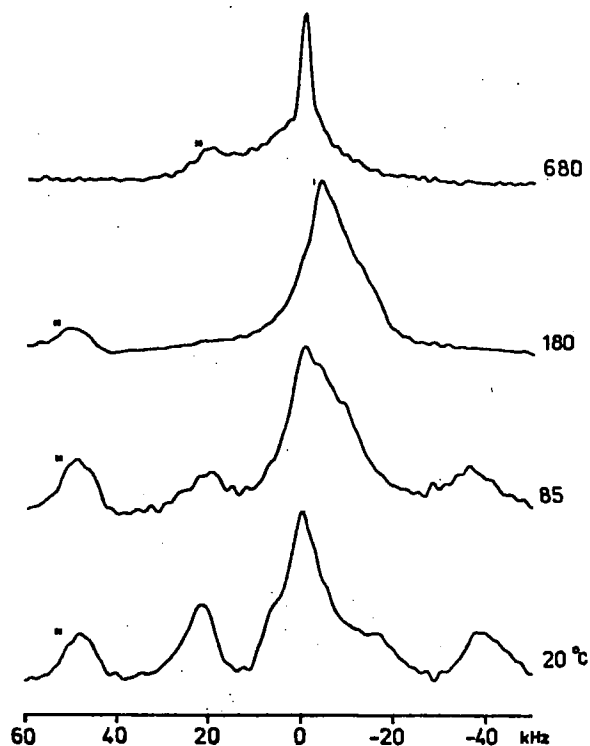
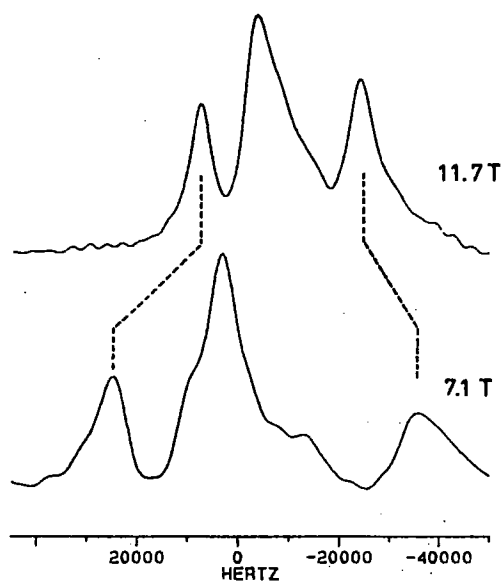


Fig. 2:  $^{23}\text{Na}$  spectra of  
zeolite NaA at two  
different magnetic  
fields.



DEPARTMENT OF BIOCHEMISTRY  
UNIVERSITY OF CAMBRIDGE

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Tennis Court Road  
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Telephone: (0223) 337733Professor Barry L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, TX 77843

(Received 1 September 1986)

Dear Barry,

**SELECTIVE EXCITATION:  
SOMETHING FOR NOTHING**

The technique of selective excitation is central to NMR imaging (1). With the advent of NMR spectrometers equipped with linear RF amplifiers there will also be important applications in high resolution spectroscopy.

We have recently developed a new numerical approach to selective pulse design. Relatively large changes can be made at each step and the method converges very rapidly, typically in a few tens of iterations. We have published a short note on the generation of a self-focusing  $\pi/2$  pulse (2). At the end of the pulse, the selected spins are all in phase and do not therefore require a hard  $\pi$  pulse or field gradient reversal in order to refocus them.

The algorithm should not be thought of simply as a method for refining selective pulses. It can be used to generate 'novel' pulses without requiring a good starting approximation. Readers may find the following example a convincing demonstration of this 'something-for-nothing property'. Figure 1 illustrates a slice-selective refocusing pulse derived in 30 iterations from a starting approximation which is identically zero. Figure 2 shows the  $M_z$  response of the selective pulse. Note that it is a genuine  $\pi$  pulse, preserving the  $M_x$  magnetization in the slice and reversing the signs of  $M_y$  and  $M_z$ .

A full account of the algorithm and examples of its wider application will be published in due course. This is a contribution from the Cambridge Biochemical NMR Group.

Sincerely yours,

J. Thomas Ngo

Peter G. Morris

Fig.1

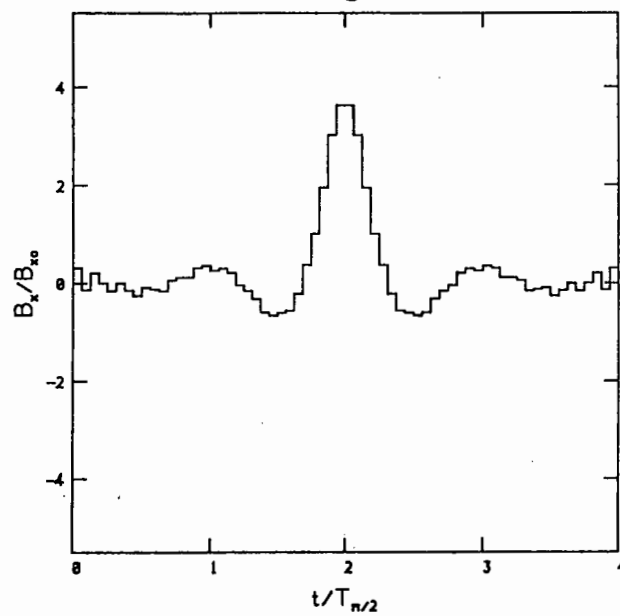
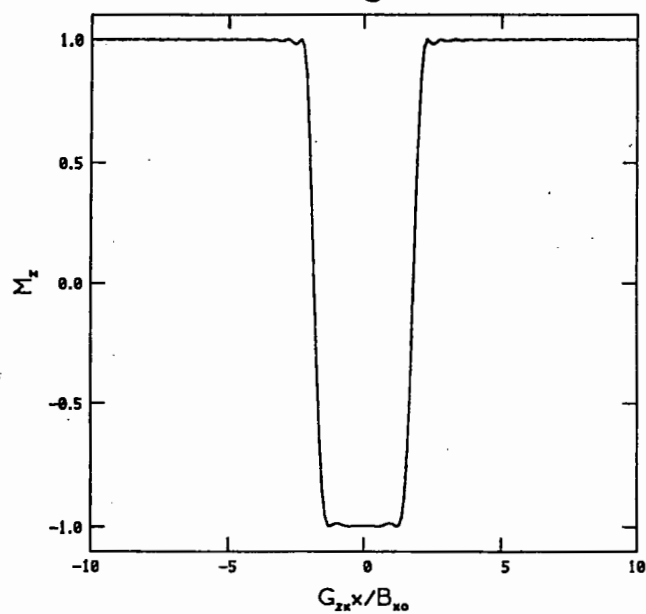


Fig.2



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- (2) J.T.Ngo and P.G.Morris, *Biochem. Soc. Trans.* 14, 1271 (1986).



## THE UNIVERSITY OF LEEDS

Department of Inorganic and  
Leeds Structural Chemistry,  
LS2 9JT, U.K.  
Telephone 431751

2nd September 1986

(Received 9 September 1986)

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

Dear Professor Shapiro,

Performance of  $^1\text{H}$  decoupling on a Bruker  
AM -400  $^1\text{H}$ - $\{^1\text{H}\}$  probe head.

We have recently been investigating the possibility of  $^1\text{H}$ - $^1\text{H}$ - $\{^1\text{H}\}$  cosy experiments as a viable alternative to  $^1\text{H}$ - $^1\text{H}$ - $\{^1\text{H}\}$  cosy experiments in the elucidation of structures in metallaborane and carbaborane chemistry and in the assignments of  $^1\text{H}$  and  $^1\text{H}$  resonances.<sup>(1)</sup> The  $^1\text{H}$ - $^1\text{H}$ - $\{^1\text{H}\}$  cosy technique has several advantages over the  $^1\text{H}$ - $^1\text{H}$ - $\{^1\text{H}\}$  cosy technique, but at present its main drawback is the difficulty to achieve efficient  $^1\text{H}$  broad band noise decoupling over the wide chemical shift range required (often more than 100ppm, i.e. 12.8 KHz on an AM-400). Our original experiments were performed on 5mm samples held in a 10mm  $^1\text{H}$ - $\{^1\text{H}\}$  probe head, observing  $^1\text{H}$  through the decoupler coil. For other reasons, we had on order a probe head for  $^1\text{H}$  observation with tunable heteronuclear decoupling. We were, perhaps naively, hoping that this probe head would provide us not only with significantly improved signal-to-noise ratios but also with a more efficient  $^1\text{H}$  decoupling performance. In the latter respect we have been rather disappointed. For an output of ca. 5W of broad band noise decoupling (the maximum recommended) we can achieve a range of ca. 100ppm for a  $^1\text{H}$  line-width of  $\leq 10$  Hz in the  $^1\text{H}$ - $\{^1\text{H}\}$  probe head. However, in the  $^1\text{H}$ - $\{^1\text{H}\}$  probe head, the decoupling range is reduced to much less than 50 ppm, which is inadequate for most compounds in which we are interested. This point is perhaps to be borne in mind by anyone else wishing to invest in probe heads for  $^1\text{H}$ - $\{^1\text{H}\}$  types of experiment.

Please credit this contribution to the account of Alistair G. Swanson,  
University of Leeds.

Sincerely yours,



Xavier L.R. Fontaine.

(1) X.L.R. Fontaine and J.D. Kennedy, J. Chem. Soc., Chem. Comm., 1986, 779.

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Dr. Walter J. Chazin, Ph.D. MB-2

Scripps Clinic and Research Foundation

10666 North Torrey Pines Road  
La Jolla, California 92037

Discrimination of Couplings  
in Triple Quantum Filtered  
COSY Spectra.

Research Institute of Scripps Clinic  
Department of Molecular Biology

Sept. 22, 1986

(Received 29 September 1986)

Dear Barry,

In the past few years, Mark Rance, Claudio Dalvit and Peter Wright have put a considerable amount of effort into a detailed examination of the performance (and occasionally, lack thereof) of a variety of multiple-quantum (MQ) and MQ-filtered (MQF) techniques on proteins. One of their standard models for these studies was the blue copper protein, french bean plastocyanin. With all this data in hand, it was high time for the formidable task of obtaining the complete sequence specific assignment of the spectrum for this 99 residue protein. Being smart, they brought in someone else for this little chore.

The assignment of this protein forms a critical foundation for a series of studies to be carried out in Peter's lab on various aspects of protein structure, dynamics, and the basic folding problem. In the next few months, the assignment process will be completed, which will allow us to return to our mounds of data to examine the relationship between various experimental parameters and the nature of the specific amino acid spin systems. As an example, the spectrum shown below demonstrates one of the very powerful aspects of the 3QF-COSY experiment, sign encoding in the multiplet structure. This property came to my rescue one day, when I identified one too many  $\alpha$  proton resonances in the region of 5.1-5.2 ppm. Upon careful examination of the 3QF-COSY, I noticed the opposite sign of one of the corresponding cross-peaks, as shown in the figure below. This reverse sign of the multiplet pattern is due to the opposite sign of the  $^2J$  direct coupling constant, thereby distinguishing this cross-peak (geminal coupling,  $^2J$  negative) from all the others (vicinal coupling,  $^3J_{\alpha\beta}$  positive). The pair of spins was subsequently identified as Pro  $\delta$  protons with chemical shifts of 3.27 and 5.14!! ppm. Proteins never cease to amaze.

Best regards,

Walter

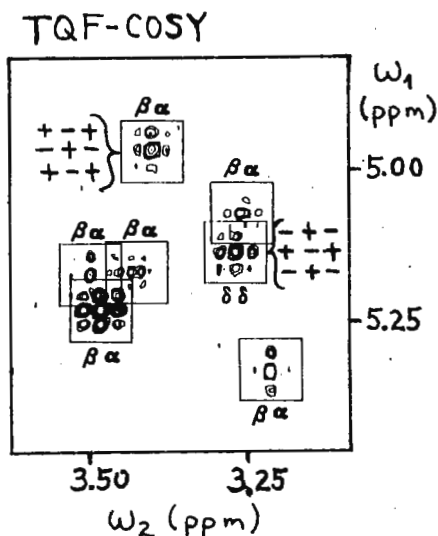
Walter Chazin

Mark Rance

Claudio Dalvit

Peter Wright

Peter E. Wright



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September 22, 1986 (Received 29 September 1986)

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

Spectral-Spatial 2-Dimensional EPR Imaging

Dear Barry:

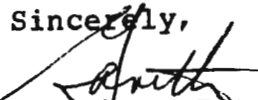
In light of the increasing frequency of NMR imaging papers in the Newsletter, we thought that some of the subscribers might be interested to read about related EPR imaging experiments that we are doing.


In the EPR spectra of organic radicals the nuclear hyperfine splittings commonly are greater than the g-value differences and so, unlike NMR, overlapping spectra are the rule rather than the exception. Therefore to image samples containing more than one paramagnetic species it is important to analyze both the spectral and spatial dimensions.

We prepared a test sample composed of two solutions in flat tubes with 0.04 cm path lengths. One tube contained a solution of galvinoxyl radical which gives a ten-line EPR spectrum. The second tube contained a solution of  $^{15}\text{N}$  tempone which gives a two-line EPR spectrum. The two tubes were positioned 0.55 cm apart. EPR spectra were obtained as a function of magnetic field gradient for 92 gradients. The first-derivative spectra were integrated. The image in the Figure was constructed using a convoluted back-projection algorithm. The horizontal axis is the magnetic field axis. The shadow of the image along this axis matches with the integral of the first-derivative EPR spectra in the absence of gradient. The vertical axis is the spatial axis. The shadow along this axis accurately reflects the fact that the spin density was localized in two regions of space separated by 0.55 cm. A horizontal slice through the image gives the EPR spectrum at a particular position along the sample. The distinctive spectra from the two samples were clearly resolved.

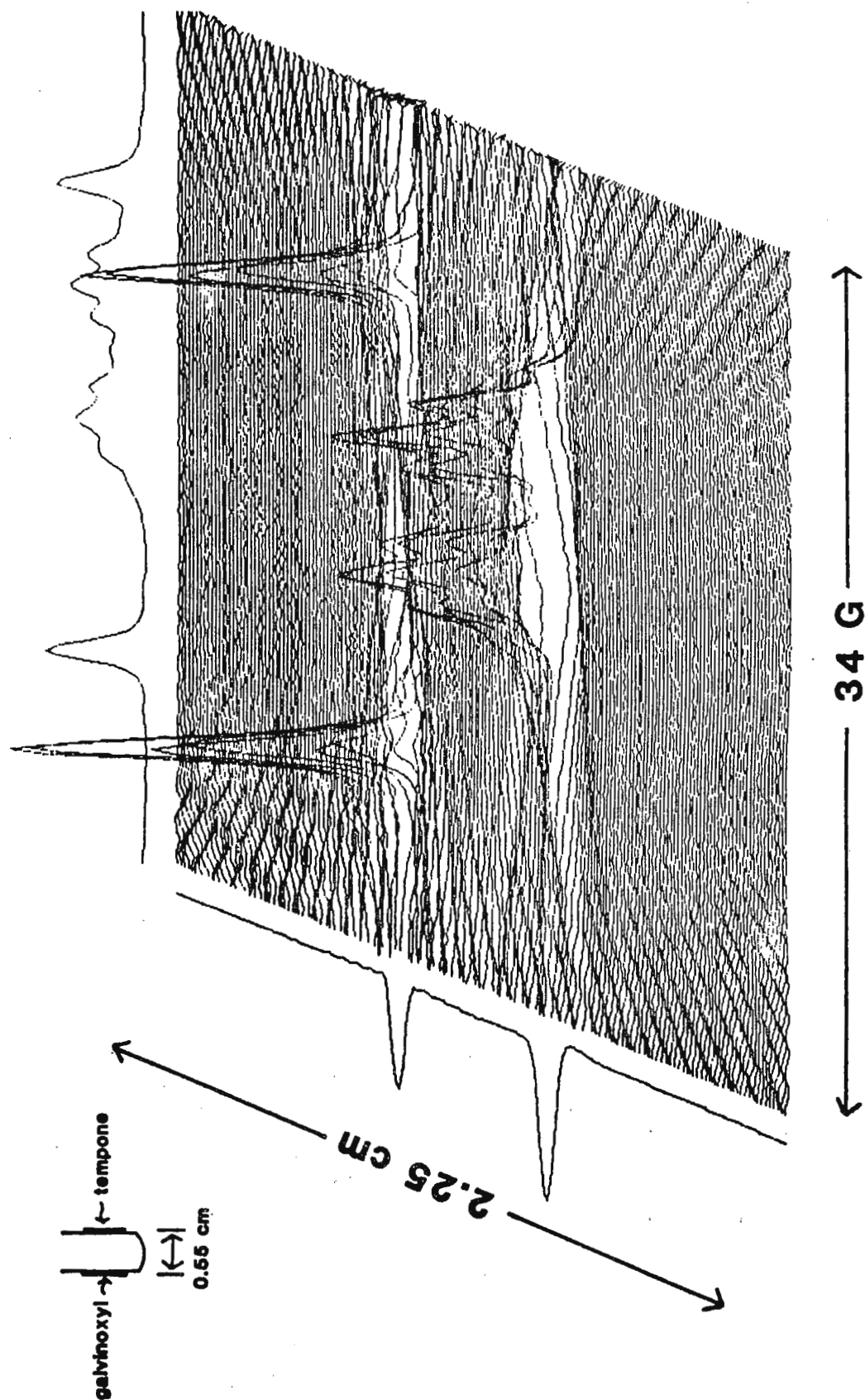
We feel that this demonstration of the feasibility of spectral-spatial EPR imaging opens up new vistas. Details have been submitted to J. Magn. Reson.

Sincerely,

  
Gareth R. Eaton  
Professor

  
Sandra S. Eaton  
Professor





# Columbia University in the City of New York

Department of Chemistry  
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Havemeyer Hall  
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Professor Bernard L. Shapiro  
Department of Chemistry  
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College Station, Texas 77843-3255

September 24 1986  
(Received 29 September 1986)

## SPIN ECHO NMR OF INTACT LENSES


Dear Barry:

Changes in lens metabolism may precede cataract formation. As a prelude to detecting these changes, Bill Garner of the Department of Ophthalmology and I have been developing methods to establish markers to monitor lens dysfunction. In order to study metabolism in the intact lens, we have been using spin echo NMR.

In this method, the spin echo delay is used as a basis for simplifying otherwise complex proton spectra, and usually limits spectral observation to small metabolites, on the basis of spin-spin relaxation times. The spin echo sequence also helps to improve the degree of solvent suppression. With a delay of 60 msec. the sequence also provides spectral editing on the basis of a nominal  $^3J_{HH}$  of *ca* 8 Hz. For the first pulse in the echo sequence we use a  $150^\circ$  pulse, as this approximates a ( $180^\circ$  - Ernst) angle, and thus improves the data capture rate in these experiments. Examination of lenses in a TC-199 medium, using the  $150^\circ - \tau - 180^\circ - \tau$  sequence resulted in several distinctive signals at 3.35, 2.4, 2.15, 1.8, 1.32 and 1.0 ppm. Tentative assignments based on model studies suggest that the major signal at 3.25 may be due to the methylene  $\beta$ -protons of cysteine in oxidized glutathione (GSSG). The prominent signal at 1.32 corresponds to lactate produced by glycolysis. This latter signal is  $180^\circ$  phase shifted because of an eight Hz coupling constant. Signals at 2.55 and 2.15 are associated with the  $\gamma$ - and  $\beta$ -glutamyl protons of GSH.

Of course, this work is at a preliminary stage but we hope that comparison of these model studies with human cataract lenses should provide a basis to follow the signals which change with opacification.

Best Wishes



C. J. Turner



UCD NMR FACILITY

DAVIS, CALIFORNIA 95616

September 10, 1986

(Received 17 September 1986)

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

Equipment for Sale

The UCD NMR Facility is in the process of obtaining a combined imaging/spectroscopy system. Therefore, we now have for sale our ORS TMR 32/200 spectrometer system. The spectrometer is operating at 1.9T and has a clear bore of 20cm with the profiling coils and 31cm without. The system has outstanding features for spectroscopy on human limbs and on organs of laboratory animals. The homogeneity is good for small volumes (linewidth of 4Hz for a sphere of 3cm diameter). The system includes apart from its standard features:

- 1) Broadband decoupler under computer control.
- 2) Profile system to control the size of the homogeneous volume.
- 3) Honeywell disk cartridge system.

The system is now regularly used an average of 6 days a week. We ask \$120,000 for the complete system, but this is of course negotiable. If you are interested please contact the UCD NMR Facility at 916-752-7677.

Jeff de Ropp

Chrit Moonen

Steve Unger

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September 23, 1986 (Received 29 September 1986)

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

Dear Professor Shapiro:

Subject: Effect of Salt Form of C-13  
Spectra of Antibiotics

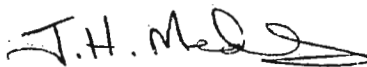
We have been studying the anthracycline antibiotic Aclacinomycin A.HCl by C-13 and proton NMR. The compound was first isolated in 1979 and the C-13 spectrum had been assigned but not the proton. It was therefore decided that the most efficient way to complete the proton assignment was via a proton-carbon 2D experiment. However, our C-13 spectra were characterized by broad lines with poor peak shapes, giving every evidence of gross contamination. The sample was assayed and found to be 98.2% pure, having 1.3% moisture and 0.5% impurity.

After attempting several different solvents and temperatures without result, it was realized that the presence of the HCl salt was causing extensive resonance in the aglycone. After neutralization with aqueous sodium carbonate and deuterium exchange, high resolution C-13 spectra were obtained consistent with the literature spectra. The 2D data was readily obtained and interpreted with the resulting proton assignment shown in Figure 1.

The take-home lesson here is to be aware of the chemistry of the formulation of a pharmaceutical material, something the spectroscopist is prone to forget.

Please credit this to the account of the Bristol-Myers Research Library. Thank you.

Sincerely,



James H. Medley, Ph.D.

jmr

cc: J. R. Allison  
E. F. McNiff





## RESEARCH SCHOOL OF CHEMISTRY

THE AUSTRALIAN NATIONAL UNIVERSITY

(Received 29 September 1986)

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 Canberra, A.C.T. 2601

Sensitivity in the ROESY Experiment

ROESY, the rotating frame analog of NOESY, offers the advantage that the cross relaxation rate in the rotating frame ( $\sigma_{\text{roe}}$ ) is a positive, monotonically increasing function of the correlation time  $\tau_c$  (1,2). In contrast,  $\sigma_{\text{noe}}$  in NOESY becomes zero at  $\omega_0\tau_c = \sqrt{5}/2$  for random, isotropic motion (3). Furthermore, the magnitude of  $\sigma_{\text{roe}}$  is expected to be at least twice that of  $\sigma_{\text{noe}}$  for slow isotropic motion (1,3), suggesting that ROESY will in general be a more sensitive experiment. This limited view of the ROESY experiment may be extremely misleading for the following reasons.

First,  $R_L^{\text{roe}}$ , the leakage relaxation rate in the rotating frame (3,4), retains a strong dipolar contribution even for systems undergoing slow motion (4).  $R_L^{\text{noe}}$ , however, is essentially independent of the dipolar interaction for an isolated  $A_nX_n$  system in this motional regime (3). Since  $R_L^{\text{roe}} > R_L^{\text{noe}}$  for systems undergoing slow motion, the increased decay rate in ROESY tempers the potential gain in sensitivity. Fig. 1 plots  $\xi$ , the absolute value of the maximum NOESY cross peak intensity relative to the maximum ROESY cross peak intensity, versus  $\tau_c$  for an isolated AX system in which magnetization exchange occurs solely through dipolar coupling. ROESY is clearly expected to be more sensitive than NOESY for this system within the range of  $\tau_c$  values typically describing macromolecular rotational diffusion. A similar theoretical plot for an isolated  $AX_3$  system (Fig. 2), however, demonstrates that intragroup relaxation may decrease ROE intensities for systems undergoing slow motion. Only for  $\tau_c$  very near the NOE cross-over point is ROESY expected to exhibit greater sensitivity than NOESY. Allowing the  $X_3$  group to undergo rapid internal rotation ( $\omega_0/4D_{||} \ll 1$ ) decreases  $\xi$  approximately 4-fold in the limit that  $\omega_0\tau_c \gg 1$  and  $r_{xx} > 2r_{ax}$  but does not substantially alter the previous conclusion. Furthermore, as one increases  $D_{||}$ ,  $\xi$  first decreases for  $\tau_c$  in the slow motion regime, but then begins to increase until the maximum  $\xi$  is obtained at  $D_{||} = D_{\perp} = D_{\text{iso}}$ . The effect of intragroup relaxation on the ROE intensity in macromolecules is therefore expected to be less severe for methyl groups, which may undergo rapid internal motion, than for equivalent spins capable of

only restricted internal motion. A more elaborate treatment and analysis of relaxation effects on the relative sensitivity of ROESY compared to NOESY will be presented elsewhere (4).

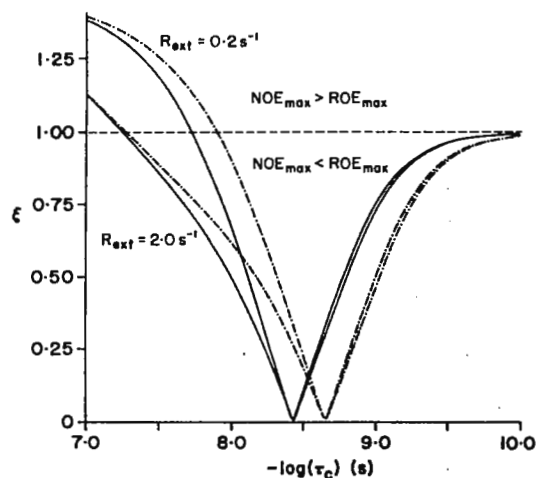


Fig. 1

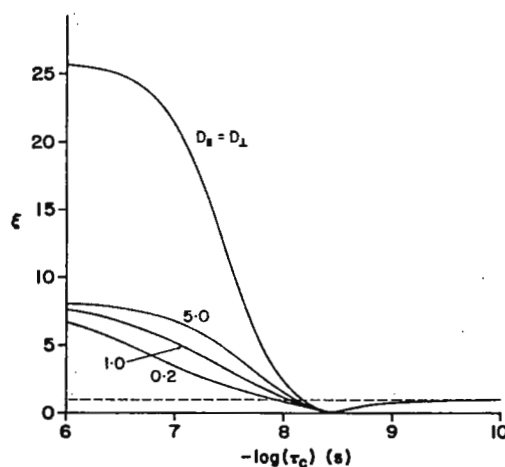


Fig. 2

**Fig. 1:**  $|\text{NOE}/\text{ROE}|$  relative sensitivity at  $\omega_0 = 300$  MHz (—) and  $\omega_0 = 500$  MHz (---) for an AX system with  $r_{ax} = 3.0 \text{ \AA}$ . The light, dashed line indicates the value for which the ROE and NOE cross peaks exhibit identical maximum intensities.

**Fig. 2:**  $|\text{NOE}/\text{ROE}|$  relative sensitivity to cross relaxation between a spin A and a methyl group ( $X_3$ ) for several  $D_{||}$  values. The A spin is assumed to lie on the rotation axis of the methyl group. Additional simulation parameters are:  $r_{xx} = 1.80 \text{ \AA}$ ,  $r_{ax} = 2.96 \text{ \AA}$ ,  $R_{ext} = 0.2 \text{ Hz}$ ,  $\omega_0 = 300$  MHz, and  $\tau_c = 1/(6D_{\perp})$ .  $D_{||}$  is expressed in GHz.

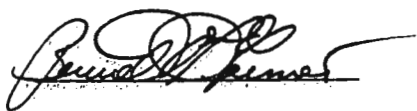
The second aspect of ROESY which diminishes its relative sensitivity is that the sign of the magnetization transferred by dipolar coupling is given by  $(-1)^n$  where  $n$  is the number of transfers (5). Since direct ( $n = 1$ ) and indirect ( $n = 2$ ) ROE transfers have opposite sign in the spin diffusion regime, their combined presence can lead to a substantial decrease in the maximum intensity of the direct ROE (4). A similar situation manifests itself in NOESY but only in the fast motion regime.

The third factor leading to a loss of sensitivity in the ROESY experiment is the Hartmann-Hahn effect (HHE) (2,4). For dipolar coupling of solely A to M' in an AMX system in which only M-X exhibits an HHE, simple considerations (6,7) predict that the maximum A-M ROE intensity will be halved. This is valid only in the limit that  $|q^{mx}/\sigma_{roe}^{am}| \gg 1$  and  $\sin^2(\phi^{mx}) = 1$  (4), where  $q^{mx}$  is the effective homonuclear HHE exchange rate and  $\sin^2(\phi^{mx})$ , the maximum efficiency of homonuclear HHE exchange attainable between spins M and X (6). In general for  $|q^{mx}/\sigma_{roe}^{am}| \gg 1$ , the maximum A-M ROE intensity is proportional to the factor  $\frac{1}{2}(2 - \sin^2(\phi^{mx}))$ . For  $|q^{mx}/\sigma_{roe}^{am}| \ll 1$ , there is no effect on the maximum A-M ROE intensity, irrespective of  $\sin^2(\phi^{mx})$ . For intermediate values of  $|q^{mx}/\sigma_{roe}^{am}|$ , the observed ROE will lie between these extremes.

In summary, the experimental  $\xi$  value for a given spin pair is expected to be highly dependent upon local geometry, local dynamics, and global dynamics. For proteins, in which equivalent, dipolar coupled spins generally abound, in which spin pairs are usually surrounded by many non-equivalent, neighboring spins, and in which the suppression of all scalar coupled, Hartmann-Hahn magnetization exchange pathways is virtually unattainable, we estimate that ROESY will offer greater sensitivity than NOESY ( $\xi < 1$ ) only for motion giving rise to a zero or near zero NOE. This motion, moreover, may arise from internal flexibility rather than the overall tumbling of the macromolecule.

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B.T. Farmer II



L.R. Brown

P.S. - Post-Doctoral Positions: We have finally received our VXR-500 spectrometer to go with the four other supercons. Consequently, I have two positions available to work on structure and dynamics of macromolecules. Airfares to and from Australia will be paid. Interested persons should send a curriculum vitae and addresses for three professional references to me (L.R. Brown) at the above address.

## NMR SPECTROSCOPIST POSITION

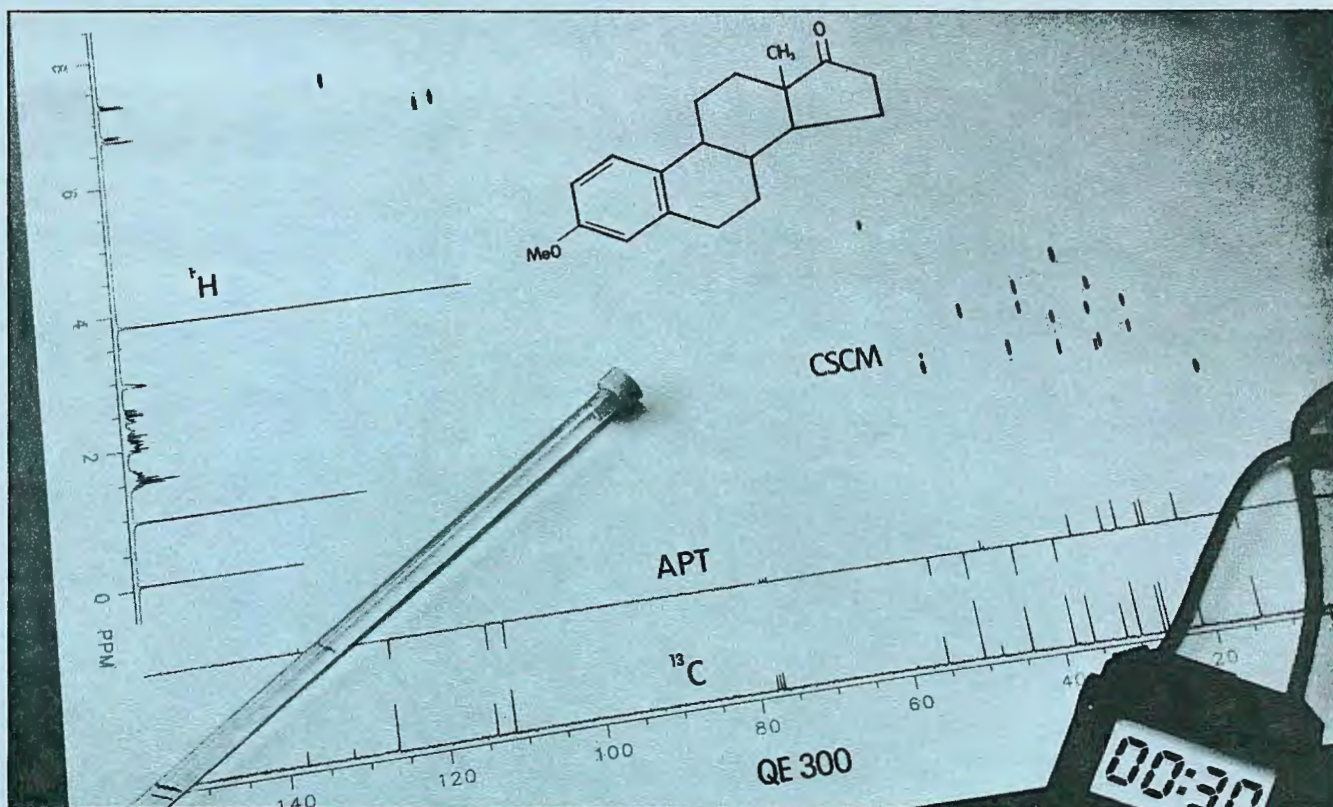
Monsanto Chemical Company has a position available for an NMR spectroscopist at its suburban St. Louis (Creve Coeur) Research Center. The position is in the Physical and Analytical Science Center, a broad range facility that provides support for R&D programs. The successful candidate will be responsible for the operation of a state-of-the-art NMR laboratory and will be involved in the study of a wide variety of products ranging from detergent chemicals to jet engine lubricants. The position offers a mix of long-range studies of new product structure, composition, and performance and shorter term projects related to product improvement, applications, and acceptability. It involves close collaboration with scientists in other disciplines as well as with support group colleagues and provides opportunities for multi-technique approaches to problem solving. The candidate must have a record of technical leadership and be able to interface well with clients, colleagues, and management. The position will involve supervision of the work of technicians.

Interested persons should contact:

Dr. Emmett F. Kaelble  
Monsanto Chemical Company, T2B  
800 North Lindbergh Blvd.  
St. Louis, MO 63167

(314) 694-4262





# GE Performance!

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

Set-up starts with *Autolock*. Lock on as little as 10%  $\text{CDCl}_3$  in a 5 mm tube.

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

After data acquisition, *Auto-phase* accurately phases  $^1\text{H}$  and  $^{13}\text{C}$  spectra.

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

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

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

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

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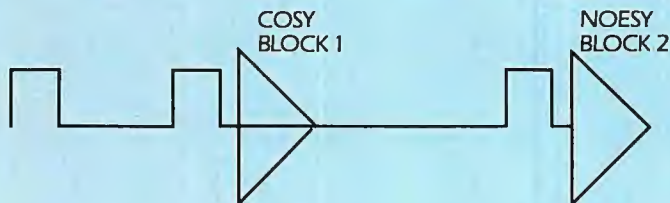
Get all the facts on the GE/NMR QE-300. Better yet, arrange for a demonstration. Call the GE/NMR group at (415) 490-8310. Or write General Electric Company, NMR Instruments, 255 Fourier Avenue, Fremont, CA 94539.

**GENERAL  ELECTRIC**

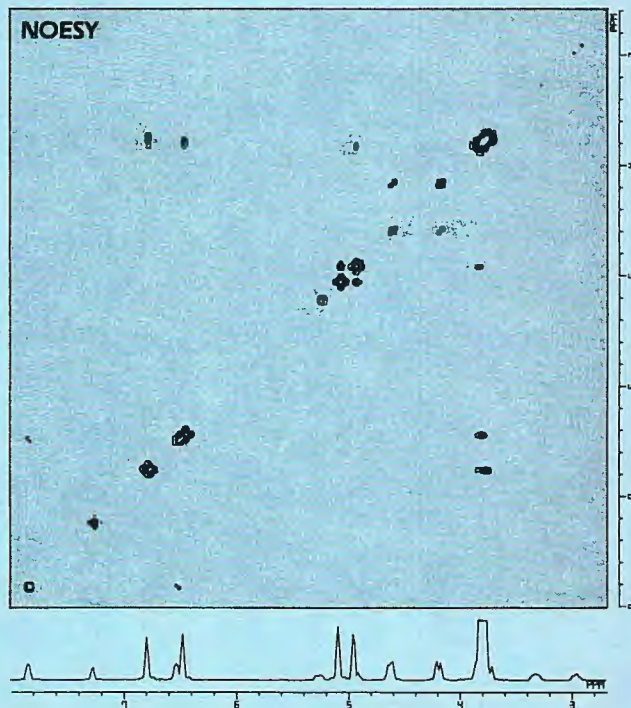
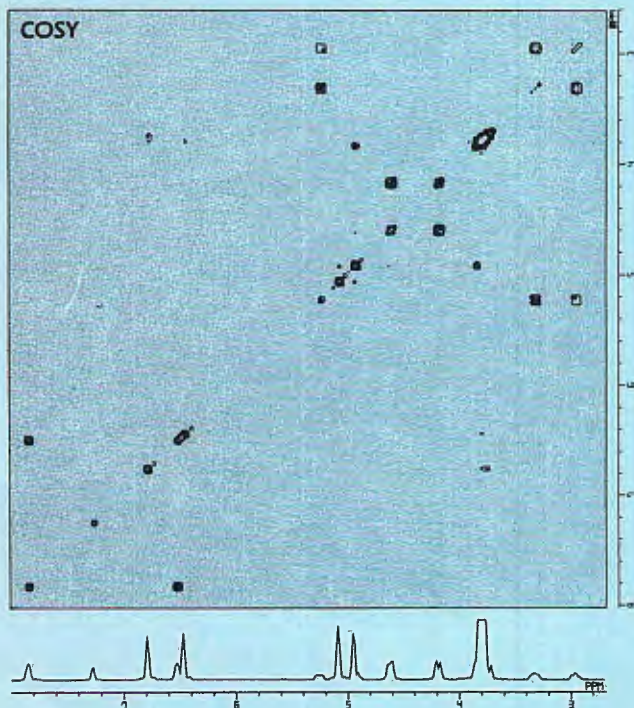


# GX Series FT NMR Systems

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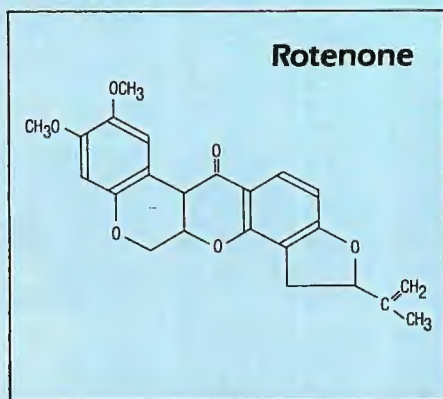


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\*COCONOSY (Haasnoot, et. al., J. Magn. Reson., 56,343 [1984])



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