THE NMR NEWSLETTER

No. 453

June 1996

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PTS 500	1-500 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$8,720.00 (1 Hz resol., OCXO freq. std.)
PTS 620	1-620 MHz	optional .1 Hz to 100 KHz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$9,625.00 (1 Hz resol., OCXO freq. std.)
PTS 1000	0.1-1000 MHz	optional .1 Hz to 100 KHz	5-10μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$11,830.00 (1 Hz resol., OCXO freq. std.)
PTS 3200	1-3200 MHz	1 Hz	1-20μs	optional	5¼"H×19"W	BCD (std) or GPIB (opt)	$14,850.00 (1 Hz resol., OCXO freq. std.)
PTS x10	user specified 10 MHz decade	1 Hz	1-5μs	standard	3½"H×19"W	BCD (std) or GPIB (opt)	$3,000.00 (1 Hz resol., OCXO freq. std.)
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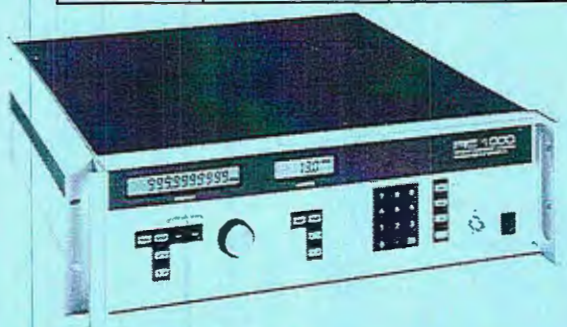

1 Switching Time is dependent on digit (decade) switched; see detailed instrument specifications.

2 For applicable digits, see detailed instrument specifications.

3 Bench cabinets are 17" wide.

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FORTHCOMING NMR MEETINGS

NMR NEXUS '96, Canadian NMR Summer School, Winnipeg, Manitoba, Canada, **June 10-14, 1996**; For further information, phone 204-984-4543; Email: nmr.school@ibd.nrc.ca; http://www.ibd.nrc.ca/; Fax: 204-984-4722.

WWW Electronic Poster Session Announcement, **June 17-21**; see Newsletter 452, 52.

NMR Symposium at the 38th Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado, **July 22-25, 1996**; Contact: Dr. Joel R. Garbow, Monsanto Company, 700 Chesterfield Parkway North, St. Louis, MO 63198; (314) 537-6004; Fax: (314) 537-6806; e-mail: jrgarb@snc.monsanto.com; See Newsletter 445, 48.

42nd International Conference on Analytical Sciences and Spectroscopy, London, Ontario, Canada, **Aug. 10-13, 1996**; Chair: M. Stillman, Dept. of Chemistry, University of Western Ontario, London, ON, Canada N6A 5B7; (519) 661-3821; Fax: (519) 661-3022; E-mail: 42info@uwo.ca.

XVIIth International Conference on Magnetic Resonance in Biological Systems, Keystone, Colorado, **August 18 - 23, 1996**; Contact: ICMRBS, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4735; Fax: (505) 989-1073. See Newsletter 452, 59.

Missouri Magnetic Resonance Symposium (MMRS) and FACSS Meeting, Kansas City, MO, **Sept. 29 - Oct. 4, 1996**; Contact: (MMRS) Frank D. Blum, Dept. of Chemistry, Univ. of Missouri-Rolla, Rolla, MO 65409-0010; 573-341-4451 fblum@umr.edu. (FACSS) 198 Thomas Johnson Dr., S-2, Frederick, MD 21702-4317.

38th ENC (Experimental NMR Conference), Orlando, FL, **March 23 - 27, 1997**; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87501; (505) 989-4573; Fax: (505) 989-1073.

4th International Conference on Magnetic Resonance Microscopy "Heidelberg Conference in Albuquerque", **Sept. 21-15, 1997**: Contact: E. Fukushima, The Lovelace Institutes, 2425 Ridgecrest Drive SE, Albuquerque, NM 87108-5127; (505) 262-7155; Fax: (505) 262-7043. See Newsletter 449, 37.

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1 May 1996

Decoupling X-Nuclei from ^{19}F on a 2-Channel Spectrometer

(received 5/13/96)

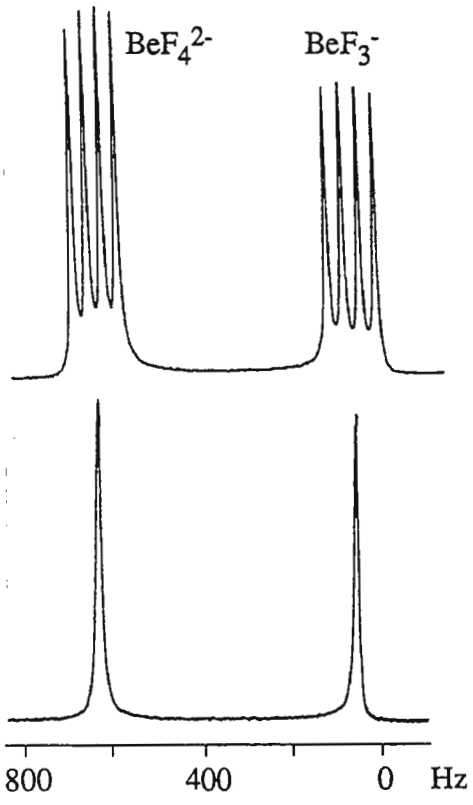
Professor B.L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry

Unfortunately we don't always have access to a multi-channel spectrometer whenever the need arises. In support of our rehabilitation we would like to relate details of a procedure we have been using for X-nucleus decoupling when observing ^{19}F on a Bruker AMX-400.

The instrument was installed with both ^{19}F and X capabilities but is controlled by the old 2-channel NMR Interface which dictates that either the observe or decoupler channel must be set to ^{1}H. However, the hardware provides all of the necessary signals for control of a (non-existent) Y-amplifier and this provides a mechanism for circumventing the ^{1}H restriction imposed on the first and second channels.

Only one frequency below ^{1}H can be generated by the primary synthesiser and we supply the X frequency from a second synthesiser (borrowed from another spectrometer) controlled by a manual frequency selection module (borrowed from another laboratory but supplied to them by Bruker). A T-connection from the 10 MHz output of the primary synthesiser provides the input to the second synthesiser whose output is fed directly to the F1 input of the BSV-10. The BSV-10 is then connected as a Y-amplifier and Router control words set to observe ^{19}F and decouple the X frequency using a BSV-10 (Y) while the BSV-10 (X) is explicitly switched off.



The ^{19}F spectrum of the beryllofluoride complexes (A.S.L. Xu, M.B. Morris and P.W. Kuchel, *Biochemistry*, 1992, **31**, 9263) shown at left was obtained on a 10 mm broadband probe with the normal ^{1}H decoupler coil tuned to ^{19}F (376.4 MHz).

The ^{9}Be decoupled spectrum shown underneath was obtained by CW(b) decoupling with dbl0 @ 36 dB (equivalent to cw with dl0 @ 36 if ROUTWD1 bit 1 is set to 1) with the BSV-10 (Y) output connected directly to the probe. Each spectrum was acquired for the same number of transients (8) and processed with the same line broadening (1Hz).

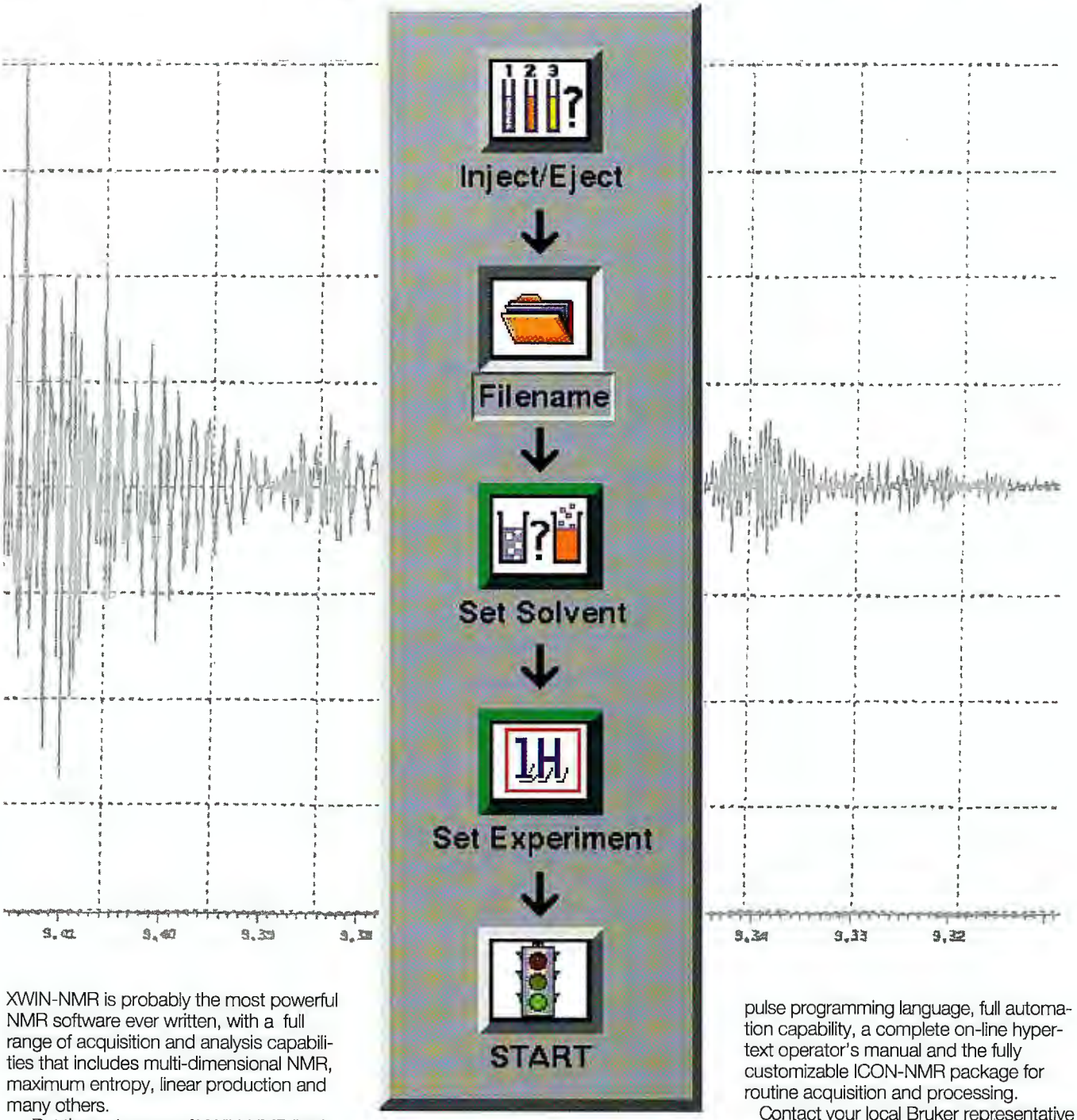
Please credit Philip Kuchel's account. We're looking forward to reading the embargoed issues.

Best regards

Bill

Bill Bubb

It doesn't get any easier than this:



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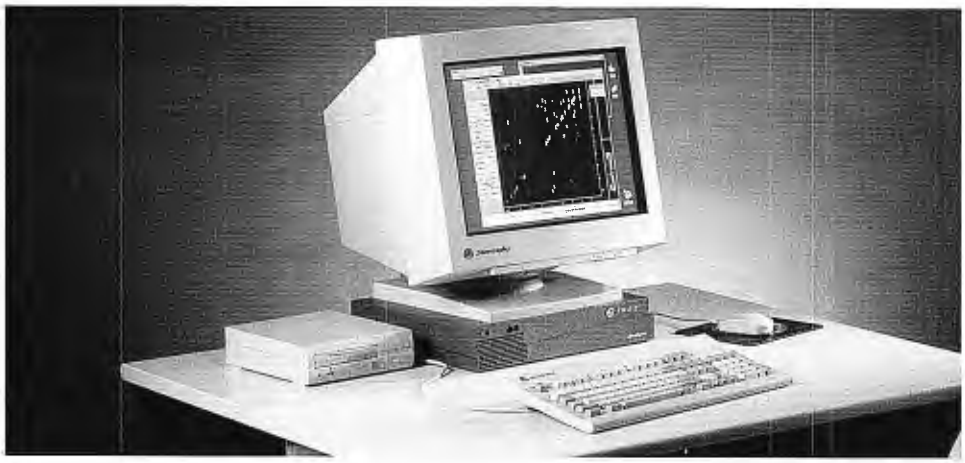

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Royal Institute of Technology
Institute of Chemistry
Division of Physical Chemistry
Dr István Furó

Stockholm 15 May 1996
(received 5/22/96)

Dr. Bernard L. Shapiro, The NMR Newsletter

966 Elsinore Court, Palo Alto, CA 94303

Title: **Report from the locksmith**

(locksmith *n* person who makes and mends locks, Oxford Advanced Learner's Dictionary)

Dear Dr. Shapiro,

We have been using field-dependent NMR relaxation measurements to study the microscopic structure of various aggregation colloids, like micelles or lyotropic liquid crystals. In many of these system the quality of the obtained structural information depends strongly on the accuracy of the spin relaxation data. Since our favoured probes have always been quadrupolar nuclei (like ^{2}H or ^{23}Na) of rather fast relaxation the instrument to map the relaxation dispersion is a field-variable electromagnet. Electromagnets require field/frequency locks and if the investigated systems are not simple liquids one has to rely on an external lock.

Until last autumn we have used a modified field-variable external ^{1}H Bruker B-SN-15 lock with a 2.1 T B-HS-90var Bruker electromagnet. The original fixed-field (2.1 T) lock has earlier been extended to operate in the 0.2 - 2.1 T range by changing the frequency source to an external frequency synthetizer synchronized with the spectrometer, by changing the transmitter to a cheap, broadband, low-power transmitter, and by replacing the receiver and the preamplifier to ones from older spectrometers. Also, we had to build new lock probes to cover the all the lock frequencies. This systems worked well but the short-time field stability was typically 3-5 Hz (measured in ^{2}H frequency, 1 Hz corresponds to ~0.16 μT) and the long-time drift was 2-4 Hz for a 10-20 hours period. We were not entirely happy with these figures and therefore tried to find the points of simple fixes. Some of these fixes were far simpler than originally anticipated! In one of the lock probes, for example, some leftover liquid and a beautiful blue crystal of copper sulfate have witnessed about a microscopic hole somewhere. Dried-out electrolyte capacitors in the power supply of the transmitter also caused some fluctuation of the lock signal.

As usual, our lock measures the period between two zero-crossings of the off-resonant lock signal. This is performed by counting pulses prepared from the 10 MHz reference; the counting is gated by a comparator applied to the lock signal. The obtained digital level is converted to an analog voltage which, together with an appropriate reference voltage, is fed into a differential amplifier whose output provides the lock-regulation signal. The NMR lock works in parallel to a flux stabilizer. First, digital noise from the lock itself added to the incoming lock NMR signal; thus the 20-50 mV noise voltage measured on the lock probe increased to ~200 mV when entering to the comparator. This extra noise has been eliminated by adding ceramic bypass capacitors. Secondly, changes have been made in counting the pulses. Originally the gated 10

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MHz pulse train was fed into a BCD counter (7490) and the output D of this counter was fed into the following DAC. This counter output counted only every 10 pulses; changing to output B and thus counting every fourth pulses increased short-term stability. The reference voltage to the differential amplifier was originally produced by a temperature-sensitive potentiometer. Thirdly, we changed it to a precise reference voltage circuit (PMI REF-2C with 1 ppm/K) which decreased the long-time drift of the field. Fourthly, the time constant of the flux-stabilizer has been optimized by adding a resistance to the input of the flux stabilizer; the optimum value minimizing the short-time noise has been around 1 kΩ.

The present typical stability is illustrated in the figure. The test experiments consist of recording the ^2H signal of heavy water at 2 MHz 256 times for 17 min (a) and 9 h (b) periods. The display of the time variation of the frequency of the half-height points of the ^2H spectrum indicates a short-time (with 4 s resolution) peak-to-peak stability of ~1 Hz and a long-time drift of less than 1 Hz. This might be worth of the (many) hours invested.

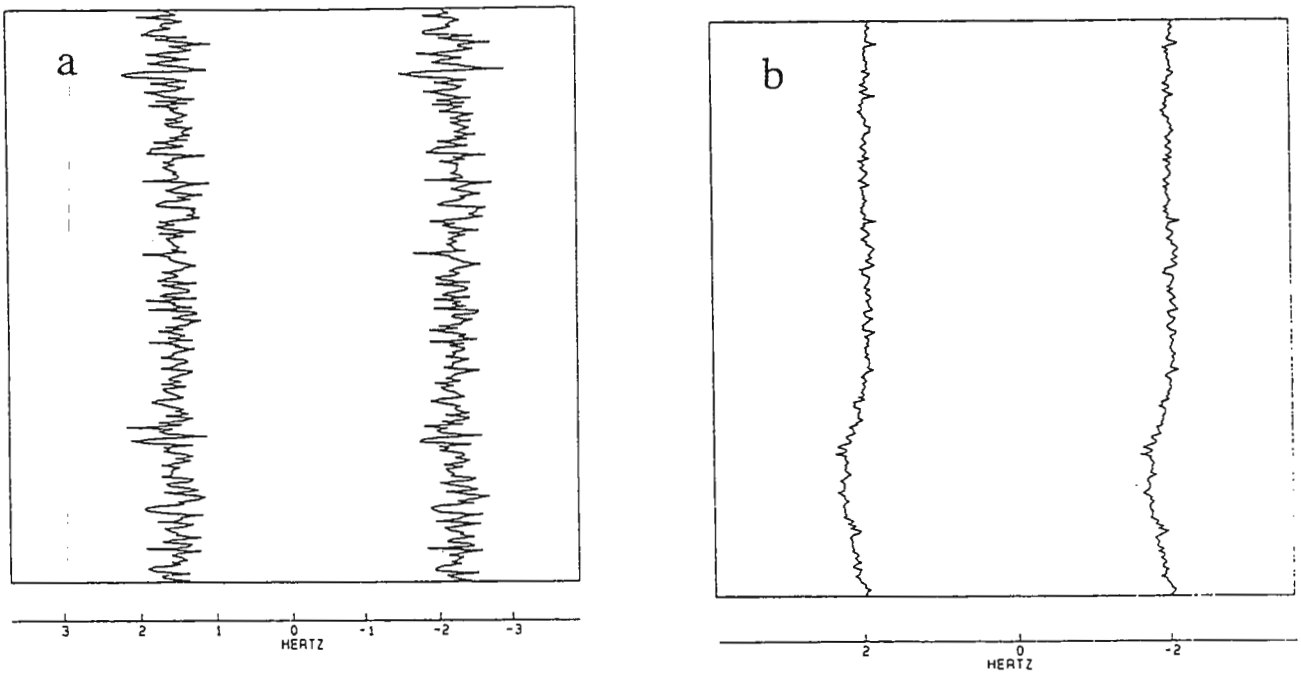
Please, credit this contribution to Peter Stilbs's subscription.

Sincerely yours

Ruslan Sitnikov

István Furó

Ulf Henriksson



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May 23, 1996
(received 5/24/96)

Dr. Bernard L. Shapiro
The NMR News Letter
966 Elsinore Court
Palo Alto, CA 94303

EASY PROCESSING OF GRADIENT-SELECTED SENSITIVITY-ENHANCED HSQC EXPERIMENTS

It has become clear that using pulsed field gradients to select coherence pathways in HSQC-type experiments is an effective way of minimizing unwanted signals. Although this approach in its simplest form results in a loss of sensitivity, modifications have been described (1) which restore full signal intensity by salvaging the signal component which is initially converted into MQ coherence by the reversed INEPT transfer step (2). In these "gradient-selected sensitivity-enhanced" experiments, two datasets corresponding to N- and P-type signals are acquired and stored separately. The original processing procedure described for obtaining a phase sensitive data set involved combination of N+P and N-P subspectra where the N-P spectrum was phase shifted by 90° before addition to the N+P spectrum (1). While this sum and difference method allows the resulting 2D subspectrum to be processed according to the method of States, et. al. (3) the complexity of this processing procedure has discouraged many spectroscopists from taking full advantage of the sensitivity enhancement scheme. We would like to point out that such data can be processed using standard coefficient tables and transform commands in Varian's VNMR software, and simple macros in FELIX.

For data acquired according to Kay et al. (1), FIDs corresponding to the two pulse sequences shown in Figures 1A and 1B are stored in alternating blocks. The VNMR command wft2d(1,0,-1,0,0,-1,0,-1) is used for generating the 2D HSQC spectrum. This procedure corresponds to an alternative strategy for combining N and P type spectra (4). In this method the N type data is reversed in ω_1 by negation of the imaginary component and then added to the P spectrum. We have found that inversion of the P spectrum by negating both real and imaginary components allows proper phase parameters for ω_2 in the 2D spectrum to be obtained by phasing the first increment in normal absorption mode. Other manipulations of the N and P spectra to form phase sensitive 2D data sets typically require either 45° or 90° phase corrections. If desired, the zero order phase parameter obtained from this VNMR processing (rp) can be used for processing in FELIX (ph0, or phase0) after being appropriately translated to account for the different sign conventions used in the two programs (phase0 = -rp). In FELIX 95.0 there is a macro called "ez2dnpgradd1.mac" which can be easily modified to conform to this mode of processing in which the phase relationship between the first FID and the 2D spectrum is the same. Figure 2 illustrates a portion of the modified macro with boxes drawn to highlight the positions where changes have been made. Figure 3 illustrates a gradient-selected sensitivity-enhanced ^{1}H-^{15}N HSQC spectrum of ^{15}N-enriched Interleukin-2 (133 amino acids). The spectrum in Figure 3 was processed using the modified ez2dnpgradd1.mac which was executed from the walking menu system of FELIX 95.0 through the path: User => E-Z 2D Transforms => D1 (t2) N/P Gradient, with phase0 = 151, phase1=0 (in this case rp=-151 for VNMR processing). After the D1 transform, the D2 dimension is transformed with: User => E-Z 2D Transforms => D2 (t1) States, with phase0=0, phase1=0. We will be happy to provide macros for processing in FTNMR 5.1 or FELIX versions: 1.1, 2.05, 2.3, or 95.0; just send a request via e-mail to fry@rnch01.dnet.roche.com. Requests for the Varian pulse sequence and parameters can be sent to: emersond@rnch01.dnet.roche.com.

Figure 1.

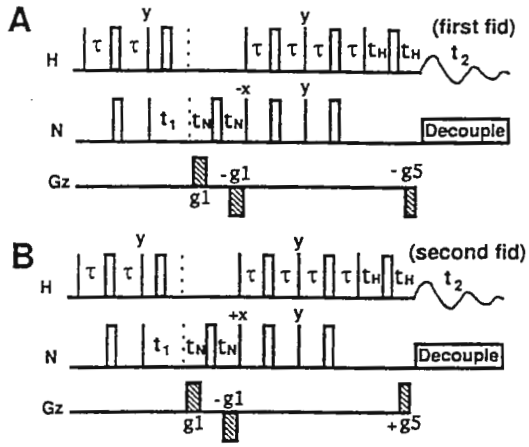
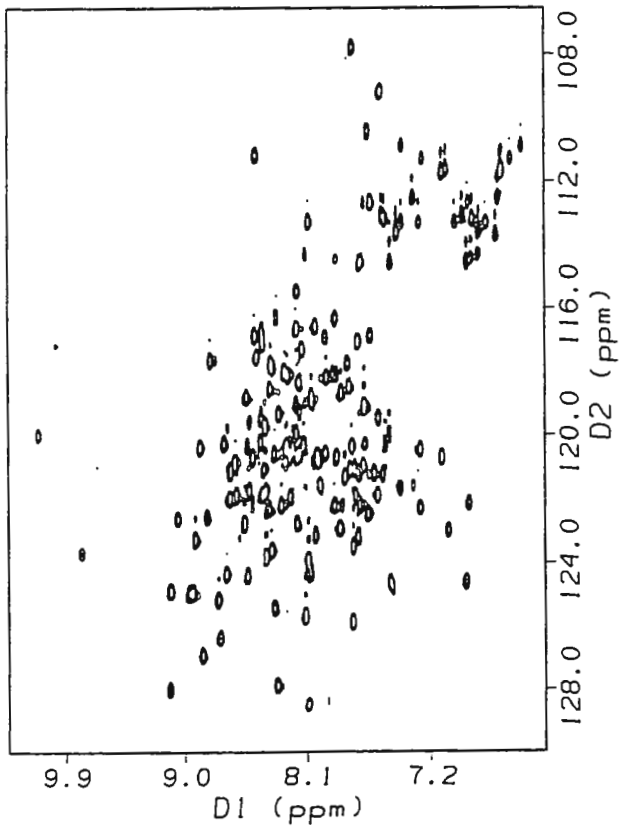


Figure 2.

```
c**ez2dnpgradd1.mac
        .
        .
        .
; D1 processing
;
   ty  D1(t2) Processing.
   ty ---------------------
;
   c1
   tim z
   for row 1 &numd1 2
     esc out
     if &out ne 0 quit
     &read &datfil
     if &status ne 0 eof
     def phase0 &temph0
     def phase1 &temph1
     def datype 1
     &dcoff
     &solfun
     &zfill
     mwb 1
     &fft
     ph
     &basfun
; Added cnj here.
     cnj
     stb 2
     &read &datfil
     if &status ne 0 eof
     def phase0 &temph0
     def phase1 &temph1
     def datype 1
     &dcoff
     &solfun
     &zfill
     mwb 1
     &fft
     ph
     &basfun
; Replaced cnj with mul -1 here.
     mul -1
     adb 2
     ldb 2
     red
     sto 0 &row
     ty Row=&row $
     ldb 2
     def datype 1
     exc
     red
     eva erow (&row+1)
     sto 0 &erow
     ty Row=&erow $
   next
 eof:
   tim r time
   if &status ne 0 then
     def status 0
     ty End-of-file on record &row
     def numd1 &row
   eif
;
   ty  D1(t2) transform completed.
   ty  Elapsed time was &time seconds.
   ty ---------------------------------
  quit:
   cmx
   def status 0
   ret
   end
```

Figure 3.



The sensitivity-enhanced gradient-selected HSQC method developed by Kay, et. al. (1) has become our preferred mode of heteronuclear detection in multidimensional experiments. The simplicity of the Nagayama type of transform (4) with the modifications described here offers straightforward processing and phasing of these datasets.

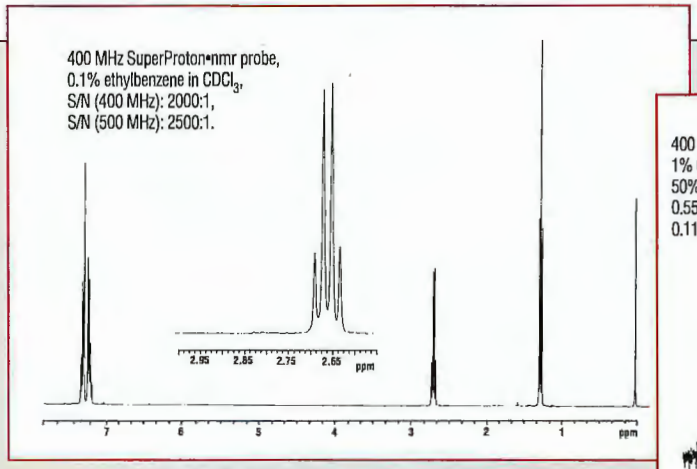
1. Kay, L.E., Keifer, P. and Saarinen, T. (1992) *J. Am. Chem. Soc.* **114,** 10663-10665.
2. Palmer, A.G., Cavanagh, J., Wright, P.E. and Rance, M. (1991) *J. Magn. Reson.* **93,** 151-170.
3. States, D.I., Haberkorn, R.A. and Ruben, D.J. (1982) *J. Magn. Reson.* **48,** 286-292.
4. Nagayama, K. (1986) *J. Magn. Reson.* **66,** 240-249.

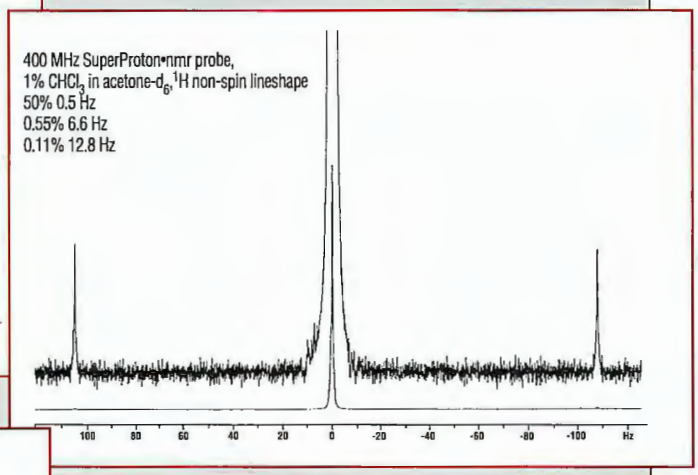
Sincerely,

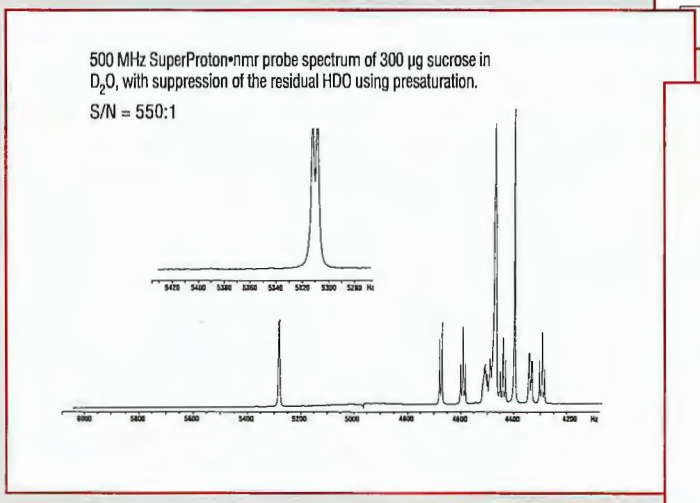
David C. Fry

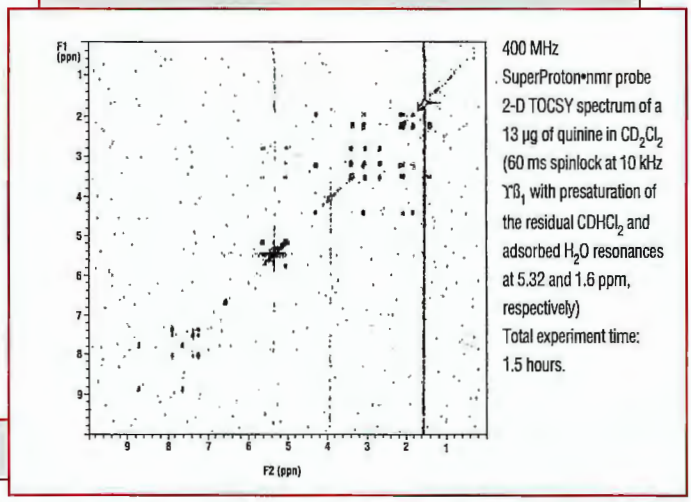
Steven Donald Emerson

Break Through the NMR Detection Limit Barrier









400 MHz SuperProton•nmr probe 2-D TOCSY spectrum of a 13 µg of quinine in CD_2Cl_2 (60 ms spinlock at 10 kHz γB_1 with presaturation of the residual $CDHCl_2$ and adsorbed H_2O resonances at 5.32 and 1.6 ppm, respectively) Total experiment time: 1.5 hours.

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Excellent RF homogeneity	High sensitivity for homonuclear experiments involving multiple pulses and pulse trains
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Dr. B.L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

May 22, 1996
(received 5/23/96)

Selective ^{1}H 2D Experiments on a Micelle-bound Membrane Protein using a UnityPlus 500

Dear Dr. Shapiro:

One of our long term interests is the structure and function of ion channels through biomembranes. Recently we began studying phospholemman, a 72 residue protein from muscle tissue that forms anion selective channels in cell membranes and phospholipid bilayers (1). The protein requires a lipid environment for stability, this requirement is satisfied during phopholemman isolation by using the detergent octylglucoside. ^{1}H 2D NMR has been used to obtain detailed structural information on several membrane proteins and peptides in deuterated detergent micelles. Unfortunately there are few readily available perdeuterated detergents and octylglucoside is not one of them. We could have tried to replace the octylglucoside with a deuterated detergent however there were a couple of disadvantages to this approach. The sample (provided by L.R. Jones, Indiana University School of Medicine) quantity was small and we did not want to suffer the inevitable loss that would occur during exchange. Also we knew that the protein was stable in octylgluoside but did not know how it would respond to other (ie. deuterated SDS or dodecylphophocholine) detergents. We decided to take an approach used by Seigneuret and Levy (2) which involved solubilizing a membrane-active peptide in octylglucoside and performing ^{1}H 2D F2 selective COSY, NOESY, and TOCSY experiments. All of the octylglucoside resonances appear between 0 and 5 ppm, therefore use of F2 selective pulses allows one to avoid excitation of the relatively intense detergent signals in the acquisition dimension. Seigneuret and Levy selectively observed the amide and aromatic (~6.5 to 9.0 ppm) region by inserting a two-frequency concatenated, shaped Dante-Z pulse train before the final nonselective pulse of the NOESY and TOCSY sequences; a similar approach was used for F2 selective COSY. Nonselective excitation of the entire spectrum would cause most of the protein resonances to be obscured by the large detergent peaks. (ie. fig. 3 of Ref. 2). We performed the same type of experiments on a sample consisting of 1mM phospholemman in 150mM octylglucoside, 90% H_2O, 10% D_2O, pH 4, however we used a Varian UnityPlus 500 spectrometer and employed a different approach to the F2 selective excitation. We replaced the final pulse of standard ^{1}H COSY, NOESY, and TOCSY sequences with the PENCE sequence of rf and magnetic field gradient pulses (3). The PENCE sequence is: nonselective 90^0_x - B_o gradient - r-SNOB$_{x,y}$ - B_o gradient - Acq$_{x,-x}$. R-SNOB is a relatively short, selective pulse for refocusing of transverse magnetization (3). The selectivity of the PENCE sequence is shown in Figure 1. Figure 1A is a 1D ^{1}H spectrum of the sample described above with presaturation of the H_2O signal and a nonselective observe pulse. Protein peaks in the amide-aromatic region are barely visible near the baseline. The PENCE sequence was used to obtain the spectrum in figure 1B. The r-SNOB excitation was centered on the amide-aromatic region and had a ~1800 Hz bandwidth. The Varian Pandora's Box software made

selective pulse setup easy. One can see that the detergent resonances are suppressed by a factor of about 150 or more. A F2 selective NOESY spectrum (mix time = 250ms) is shown in Figure 2. Note the lack of artifacts due to residual detergent intensity. Comparison of our Fig. 2 with Fig. 3b of Ref. 2 suggests that we may be obtaining more complete suppression of detergent peaks.

The cross peak linewidths (>10 Hz) in NOESY and TOCSY were somewhat larger than would be expected for a 72 residue protein and few TOCSY multiple bond transfers were observed. These observations were consistent with gel electrophoresis results which showed that most of the protein had dimerized. Observation of extensive overlap in the amide - αH cross peak region and the probable dimerization of the protein indicate that ^{15}N labeling of the protein is an appropriate next step.

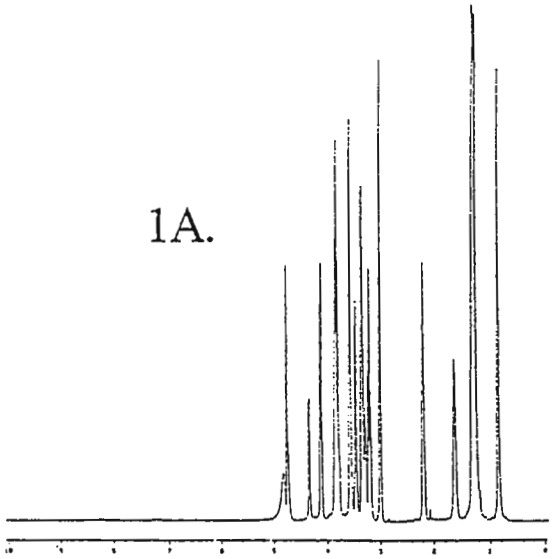
Thanks to R.G. Bryant of the UVa Chemistry Department for allowing us to use his UnityPlus spectrometer.

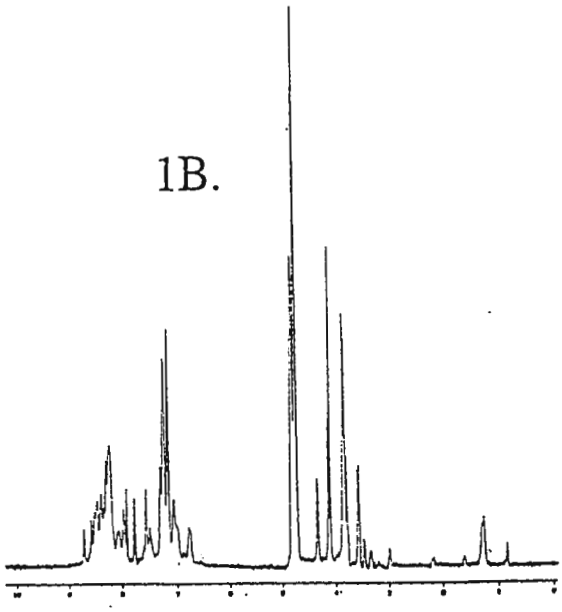
1. Moorman, J.R. et al., Nature **377**, 737-740 (1995).

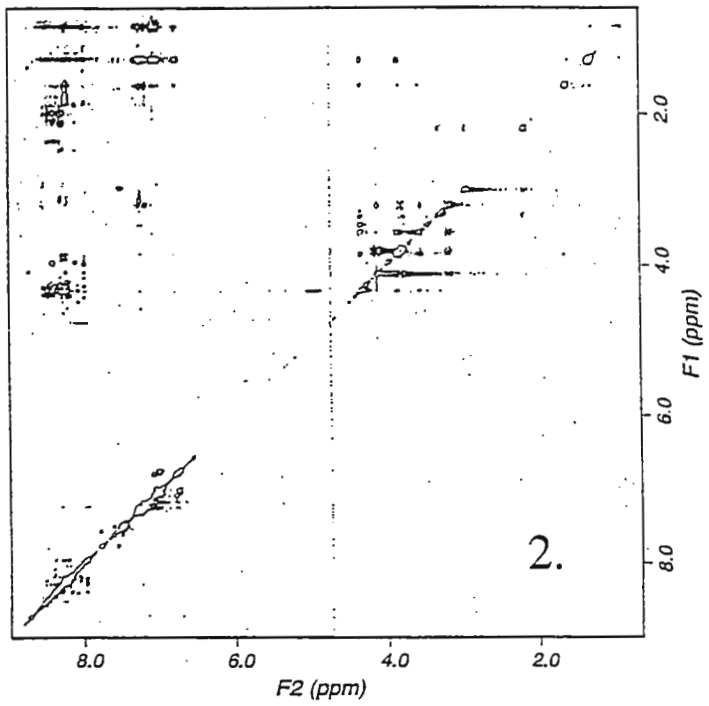
2. Seigneuret, M. and Levy, M., J. Biomol. NMR **5**, 345-352 (1995).

3. Kupce, E. et al., J. Magn. Reson. **B106**, 300-303 (1995).

Jaison Jacob Jeff Ellena David S. Cañiso







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

THE UNIVERSITY OF UTAH

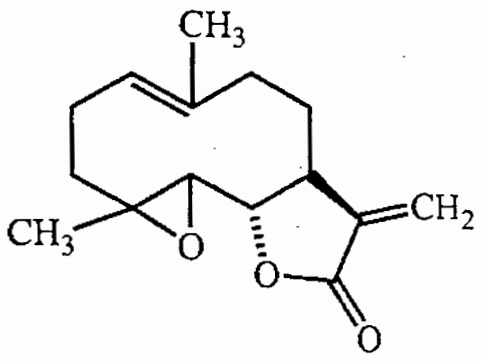
(received 5/4/96)

Characterization of chemical shift anisotropy in natural products: new applications of the PHORMAT experiment

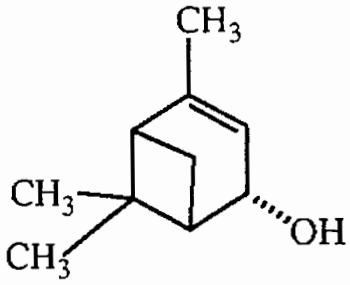
Dear Dr. Shapiro

A new 2D solid state NMR method, PHORMAT, has been used since 1995 for obtaining principal shift tensor values[1]. This method appears to solve many of the problems encountered in previous solid state powder methods[2] and allows an unusually large number of atoms to be characterized in a single spectrum. We have recently focused on applications of ^{13}C PHORMAT to bioactive terpenes to further exhibit the abilities of this method, in which principal shift tensor values for all carbons in a large molecule are obtained.

The molecules, parthenolide and verbenol, studied were selected because they contain a significantly larger number of carbons than are usually possible to study by alternative solid powder methods.



Parthenolide



Verbenol

The difficulties caused by the numerous atoms were further complicated by the fact that parthenolide had nearly twice the number of ^{13}C signals expected, consistent with two non-symmetry related molecules in the asymmetric portion of the unit cell found by x-ray analysis. In spite of these difficulties, PHORMAT successfully obtained nine clearly resolved

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powder patterns in the verbenol spectrum and 25 patterns in the spectrum of parthenolide. Coincidental overlap of certain isotropic signals obscured some powder patterns in each molecule. Principal values, along with statistical measures, were obtained for all resolved patterns by fitting algorithms. A typical PHORMAT spectrum of parthenolide is shown in figure 1.

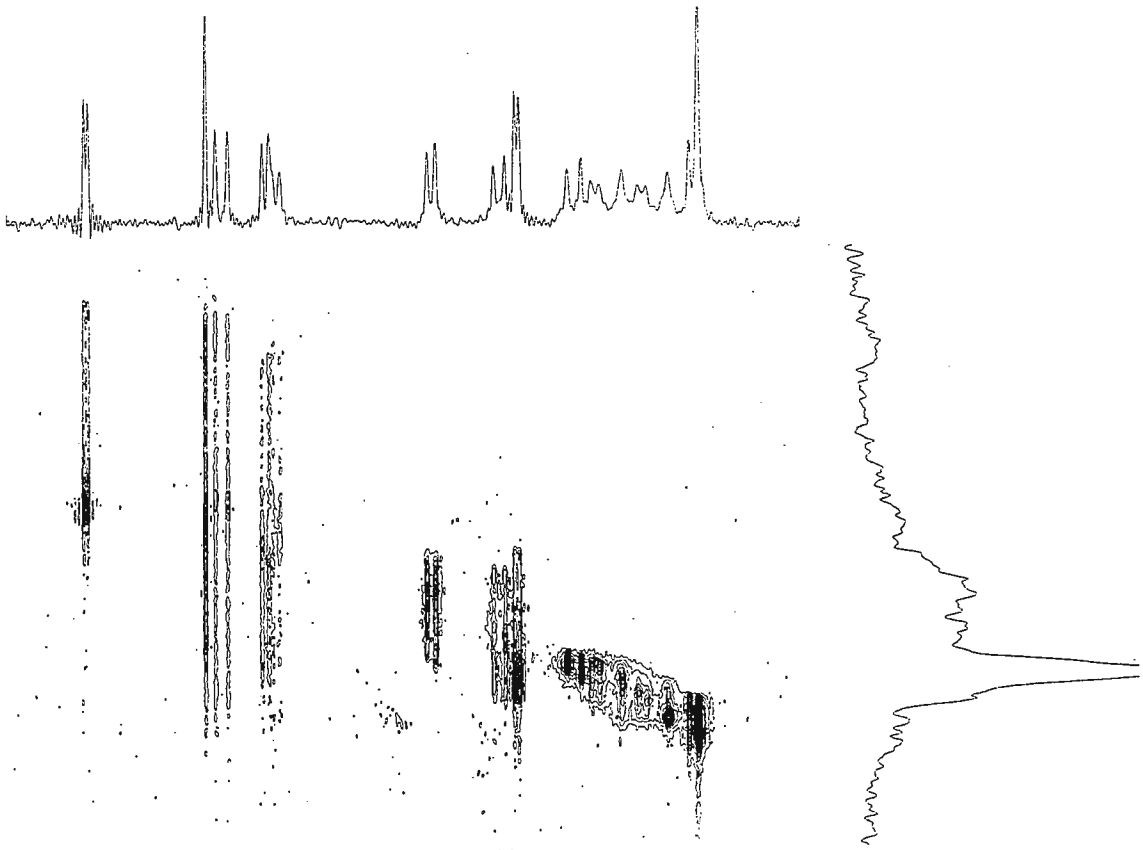

Figure 1.

Since tensors are a very sensitive reflection of molecular structure, the ability to obtain tensor principal values for all atoms in a structure is extremely desirable. The PHORMAT experiment can clearly provide such data.

Sincerely,

James Harper

James Harper

Dave Grant

David M. Grant

1. Hu, J. Z.; Wang, W,; Liu, F.; Solum, M.; Alderman, D. W.; Pugmire, J.; Grant, D. M. *J. Magn. Reson. A* **1995**, *113*, 210.
2. Orendt, A. M. In "Encyclopedia of Nuclear Magnetic Resonance:; Grant, D. M.; Harris, R. K.; Eds.; Wiley: New York, 1996; Vol. 2, p 1282.

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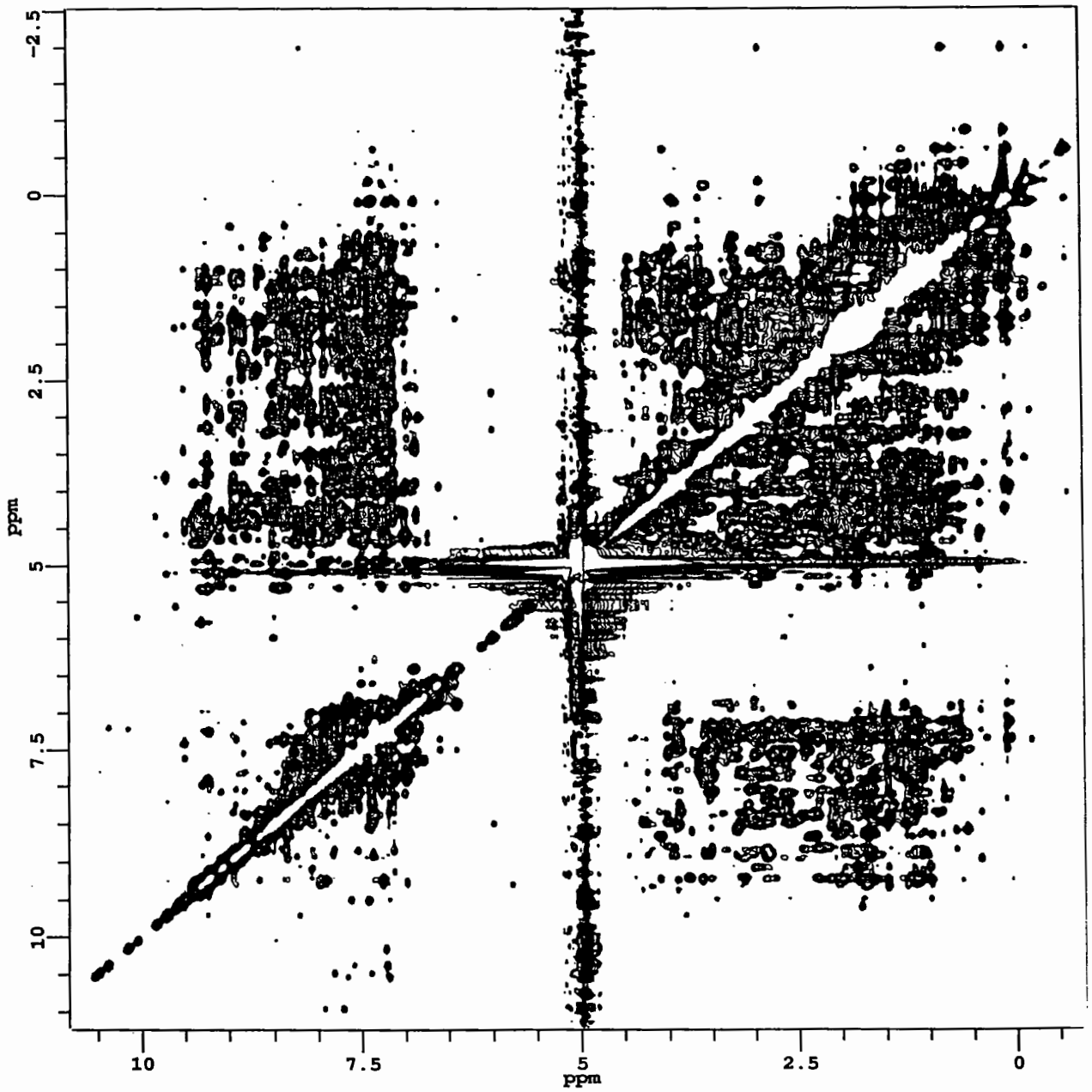

WATERGATE NOESY SPECTRUM OF LYSOSYME

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Faculty of Chemical Technology and Materials Science
Laboratory of Organic Chemistry and Catalysis
Julianalaan 136, 2628 BL Delft
The Netherlands

Delft, May 7, 1996

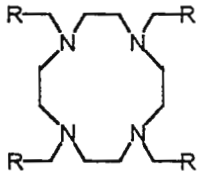
(received 5/23/96)

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

NMR Study on the Inclusion Compounds formed between Tm(DOTA)⁻ and γ-Cyclodextrin

Dear Dr. Shapiro,

Inclusion compounds with cyclodextrins have been widely studied, and a number of them have practical applications.[1] Gd(DOTA)⁻ is extensively used in biomedicine as a contrast agent for Magnetic Resonance Imaging (MRI). By forming an inclusion compound as an adduct with a cyclodextrin molecule, the biodistribution of a lanthanide complex can be altered *in vivo* and the properties to serve as contrast agents can be improved.



DOTA: R= -COOH

DOTP: R= $-PO_2H_3$

Previously, Sherry *et al.*[2] reported an NMR study on the inclusion complex formed between γ-cyclodextrin (eight α-1,4-linked glucose units) and $Tm(DOTP)^{5-}$ (Fig. 1). The association constant determined was rather small (about 4 mol l^{-1}). We report here an NMR study of the host-guest compound formed between γ-cyclodextrin and Tm(DOTA)⁻. This complex is smaller than $Tm(DOTP)^{5-}$ and can form a more stable inclusion compound.

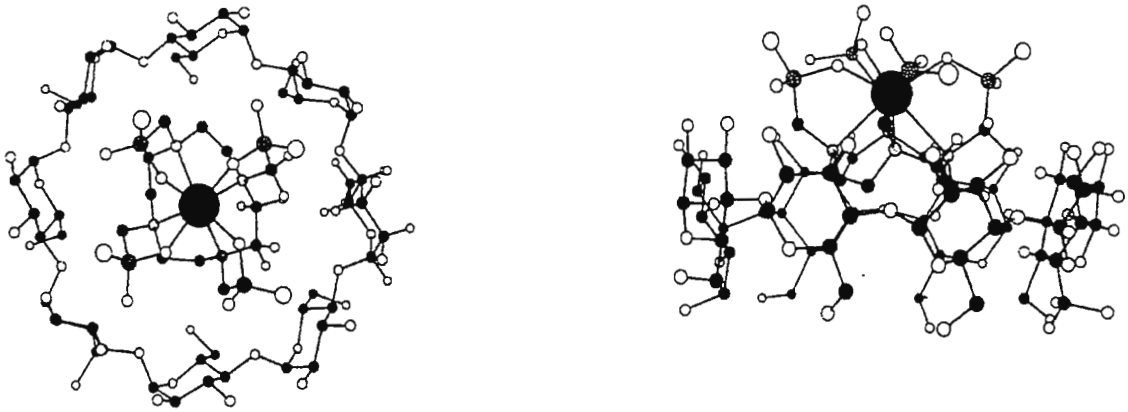


Figure 1: γ-cyclodextrin:$Tm(DOTP)^{5-}$ inclusion compound, top and side view[1]

Lanthanide Induced Shifts (LIS)

By titrating a solution of γ-cyclodextrin (γ-CD) with Tm(DOTA)⁻, the proton resonances of the cyclodextrin molecule were paramagnetically shifted, some to higher others to lower frequencies (Fig. 2). The magnitude of the shift of every proton is proportional to the amount of Tm(DOTA)⁻ in solution, indicating that free and bound γ-CD are in fast exchange.

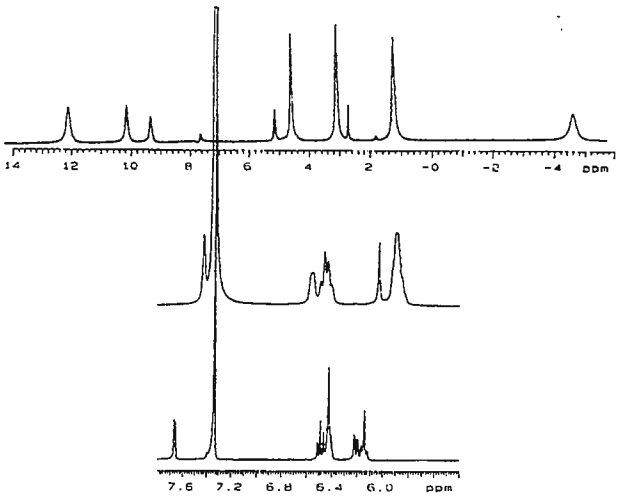


Figure 2: ^{1}H-NMR spectra of γ-CD + Tm(DOTA)$^-$ at ρ=0 (a), 1:1 (b), and 1:7.5 (c)

Remarkable is that the Lanthanide Induced Shifts for the cyclodextrin protons are not reaching a limiting incremental shift, even at a molar ratio γ-CD:Tm(DOTA)$^-$ 1:7.5 (Fig. 3). This can be due to a very small association constant for the host-guest complex. Computer simulations indicate that a 1:2 γ-CD: Tm(DOTA)$^-$ compound is formed.

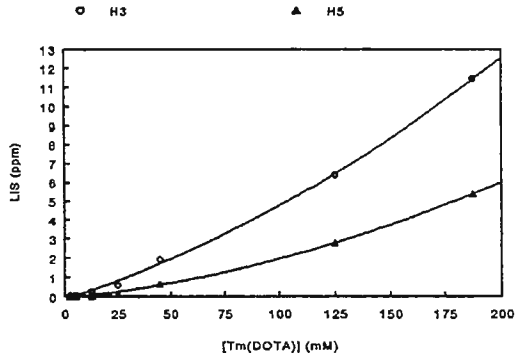


Figure 3: LIS *vs.* [Tm(DOTA)$^-$]

Relaxation Times

From the measured ^{1}H and ^{13}C relaxation times we calculated the relative distances of the various host nuclei to the paramagnetic center (the relaxation rate is inversely proportional to r^6). The protons H_3 and H_5, both located in the inside of the cyclodextrin cavity, are closer to the Tm^{3+} ion compared to the other protons. This leads to the tentative structure for the 1:1 complex as reported by Sherry *et al.*[2] and shown in Fig.1; one Tm(DOTA)$^-$ complex is located above the center of the cyclodextrin cavity. The position of the second Tm^{3+} complex is not yet determined.

1. W.Saenger, *Angew.Chem.Int.Ed.Engl.* **19**, 344 (1980)
2. A.D.Sherry, R.Zarzycki, and C.F.G.C. Geraldes *Magn.Res.Chem.* **32**, 361 (1994)

Sincerely,

Emrin Bovens Herman van Bekkum Joop A. Peters Carlos F.G.C. Geraldes

Villeurbanne, 9 May 1996

Laboratoire de Résonance Magnétique Nucléaire
Méthodologie et Instumentation en Biophysique
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Prof. B.L. SHAPIRO
The NMR Newsletters
966 Elsinore Court
Palo Alto CA. 94303

(received 5/17/96)

Back projection imaging with normal ^{3}He

Dear Professor Shapiro,

The high values of translational diffusion coefficients in gases may represent an impediment for ^{3}He (or ^{129}Xe) imaging of cavities. Then it is judicious to operate with high static field uniformity and using low gradient intensity. A further improvement is to employ back-projection in order to reduce the application time of gradients. We report here one of our first observations and our first image with normal ^{3}He at 2Tesla (horizontal here) and using the back projection technique. (Figures 1 and 2). An inductively coupled double loop resonator with vertical axis was employed.

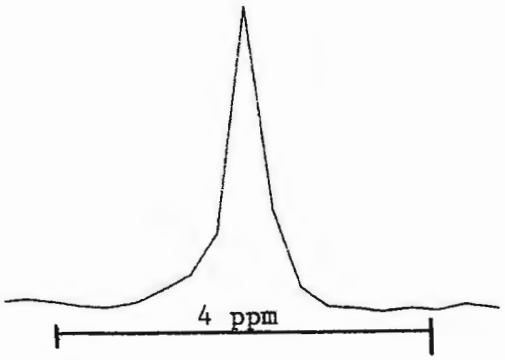

Figure 1 : single scan at 64.85 MHz (sample : pyrex vial, diameter 2.3 cm height (along 0y) 4 cm containing ^{3}He at atmospheric pressure)

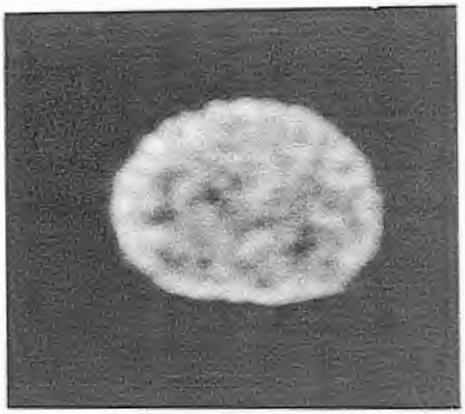

Figure 2 : 2D backprojection in the z0x plane (60 profiles, averages number 8, gradient value 2.5 mT/m, total acquisition time 13 h)

We thank Professor I. Berkès [Institut de Physique Nucléaire, Lyon] for kindly providing the ^{3}He sample.

Yours sincerely,

A BRIGUET Y.CREMILLIEUX A.DEGUIN M.VIALLON

The NMR Newsletter - Book Reviews

Book Review Editor: **William B. Smith**, Texas Christian University, Fort Worth, TX 76129

Magnetic Resonance in Perspective:

Highlights of a Quarter Century.

Edited by

Wallace S. Brey

Academic Press, Inc., 525 B Street, Suite 1900, San Diego, CA 92101-4495 1995, or
24-28 Oval Road London NW1 7DX, U.K.
1996. ISBN 0-12-133145-8 (Hbk). 681 pages. $59.95.

This volume is a collection of some fifty-five articles drawn from the pages of the *Journal of Magnetic Resonance*. The selection was made by Editor Wallace Brey, his Editorial Board and selected friends. As pointed out in the Editor's introduction, the first NMR experiments on bulk matter occurred in 1945 and *JMR* came into existence in 1969. Thus, the period covered by these articles (1970-1990) represents nearly half of the lifetime of this discipline. The idea was to celebrate the fiftieth year of NMR and the major contributions which have been made by the various authors to this Journal. It is of course obvious that the authors of these selections have been, and often still are, the leaders in the field. It is of interest to note that many of the early Mitarbeiter are now leaders themselves.

Any attempt to list all the articles and authors would be prohibitive, but let it be said that the first article (NMR Spectra of Reorienting Nuclear Pairs in Solids: Application to Conformational Changes) by E. R. Andrew and J. R. Brookeman and the final article (Gradient-Enhanced Spectroscopy) by R. E. Hurd serve as bookends for a wealth of important and interesting works which have changed the role and scope of NMR spectroscopy. By head count, the two leading contributors to this volume are Ray Freeman (12 articles) and Richard Ernst (8 articles).

Those who have followed developments in the field closely over the period covered will find many old friends here. Newer workers who find it hard to keep up with the current literature will find a compendium of articles describing how we have arrived at the current state of the art. Some will find articles which slipped through the cracks. This volume offers something of interest to all workers in the NMR field. A comprehensive five page index is included.

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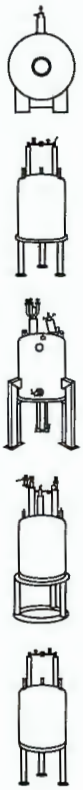

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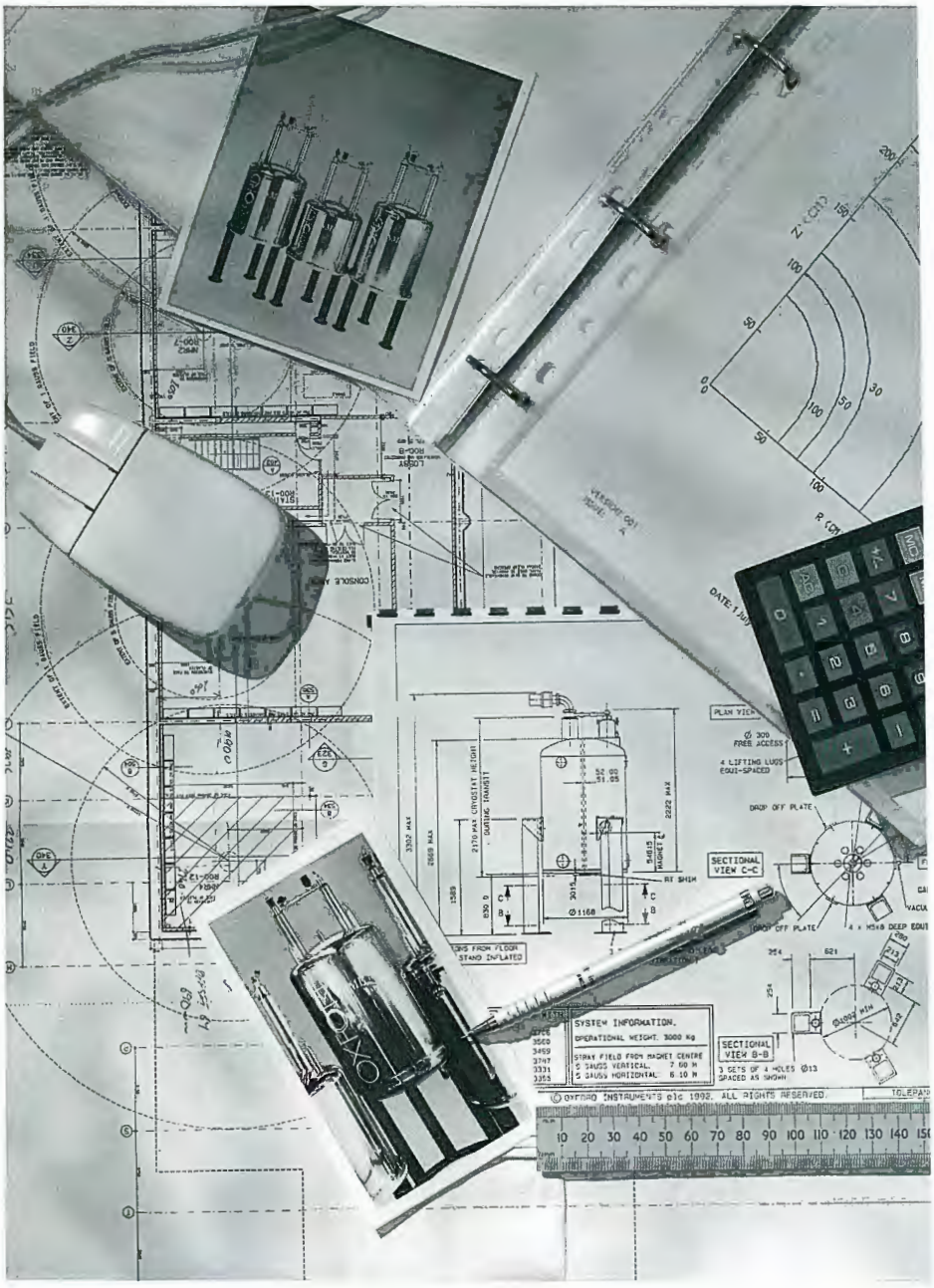

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600	51	10	120	3.4
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400	54	8	365	2.8
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300	54	3	365	2.8
270	54	2.7	365	2.8
200	54	2	365	2.8
100	54	1	365	2.8
500	89	15	120	3.4
400	89	10	180	2.8
360	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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NORTHWESTERN UNIVERSITY

May 8, 1996
(received 5/13/96)

Joseph B. Lambert
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Dr. Bernard L. Shapiro
The NMR Newsletter
966 Elsinore Court
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Dear Barry:

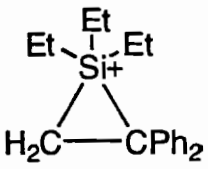
Silicon is well known for its ability to stabilize positive charge on carbon at the beta position, as in the general structure Si-C-C^+. Such a cation has been studied as a reactive intermediate and exploited synthetically for its directing ability. To date, no long-lived examples have been reported in condensed phase. Rapid decomposition occurs by attack of any available nucleophile at silicon. Loss of silicon generally leads to alkenic products. The thermodynamic stability of $Me_3SiCH_2CH_2^+$, however, is not in doubt, as Squires and others have examined its properties in the gas phase. Failures in condensed phase therefore must be kinetic rather than thermodynamic.

We now have obtained NMR evidence for the species $Et_3SiCH_2CPh_2^+$, which shows no sign of decomposition at room temperature over several days. Our strategy was to minimize the nucleophilicity of the anion and the solvent. Following methodology we developed for approaches to silylium ions, we used tetrakis(pentafluorophenyl)-borate, $(C_6F_5)_4B^-$ or $TPFPB^-$, as the anion and benzene or toluene as the solvent. We prepared the highly colored β-silyl carbocation by the addition of solvated triethylsilylium TPFPB to 1,1-diphenylethene:

$$Et_3Si^+(benzene)\ \ TPFPB^- + H_2C{=}CPh_2 \rightarrow Et_3SiCH_2CPh_2^+\ \ TPFPB^- + benzene$$

The ^{13}C spectrum (Figure 1) contains peaks diagnostic of a carbocation. The resonance at δ 225.4 indicates that most of the positive charge resides on the phenylated carbon. The methylene resonance at δ 56.2 is 26 ppm higher frequency than the methyl carbon in $MePh_2C^+$. Normally, silylation results in a shift to lower frequency. The high frequency ^{29}Si resonance at δ 46.2 indicates some positive charge on silicon. The ^{13}C DEPT spectrum (Figure 2) confirmed these structural conclusions. Low polarization transfer to unprotonated carbons eliminates resonances from the fluorinated aromatic carbons in the anion, the ipso aromatic carbon in the product, the carbocationic carbon, and deuterated solvent. The methyl subspectrum contains only the carbon of the ethyl groups, the methylene subspectrum contains the other carbon of the ethyl groups as well as the carbon adjacent to the phenylated carbon, and the methine subspectrum contains the non-ipso aromatic carbons and some residual, undeuterated solvent.

The spectral characteristics agree entirely with the open structure $Et_3SiCH_2CPh_2^+$ and not with the alternative bridged form: The open structure is stabilized through hyperconjugation (Et_3Si-CH_2-$CPh_2^+ \longleftrightarrow Et_3Si^+\ CH_2{=}CPh_2$), resulting in shared charge on both carbon and silicon.



Sincerely,

Joseph B. Lambert

Yan Zhao

Title: A Stable β-Silyl Carbocation

FIGURE 1

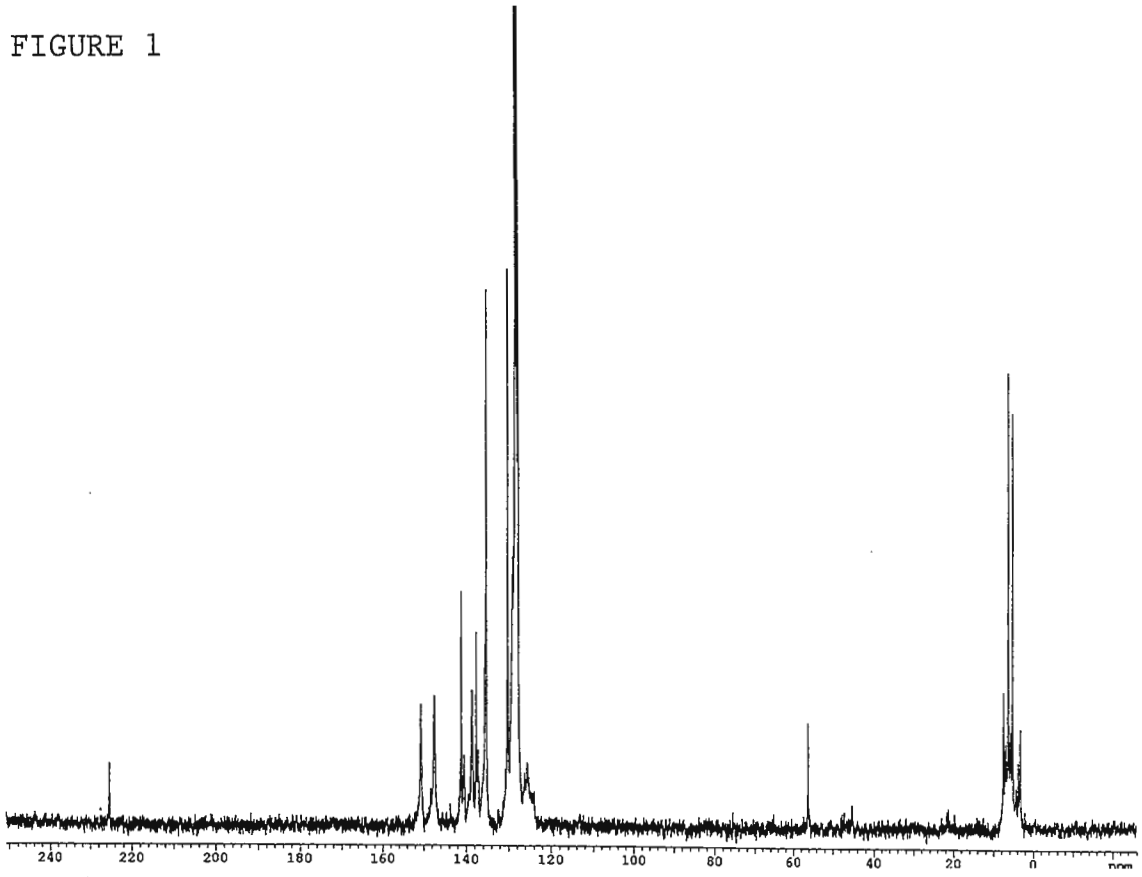
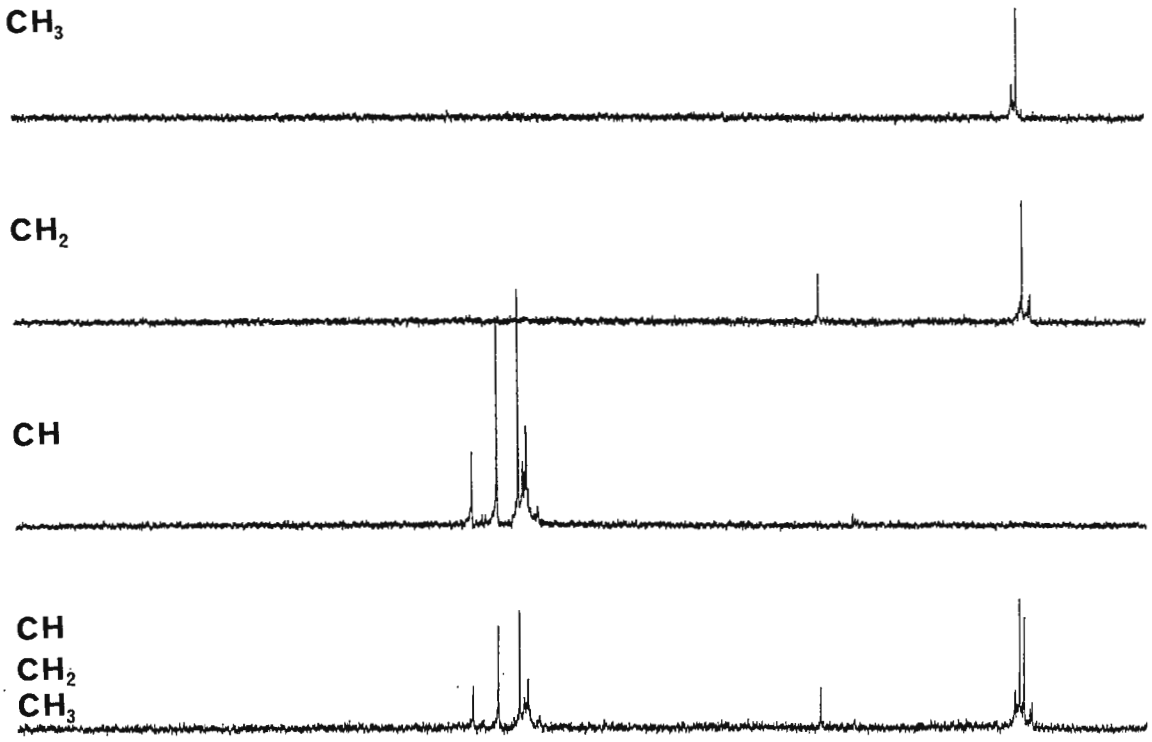


FIGURE 2



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May 7, 1996
(received 5/9/96)

Temperature Woes

Dear Barry,

Accurate temperature control is a prerequisite for meaningful results in NMR studies of molecular dynamics. If the sample is in a stable condition and the electronics are functioning and correctly calibrated then the difference between the set temperature and the actual temperature of the NMR sample can only arise from two sources. The first cause is rf induced sample heating, especially in samples of high ionic strength (e.g., 1). A second and more fundamental source of error is if the thermocouple doesn't sense the part of the probe where the sample is positioned.

In some preliminary molecular dynamic experiments on our Bruker DRX 300 using a 5 mm inverse probe we obtained some rather anomolous results. In these experiments we had (erroneously !) assumed that the set temperature on the VT-2000 temperature control unit was a reasonably accurate guide of the actual sample temperature (we expected ± 1 K). However, further investigation using methanol and ethylene glycol NMR thermometers (e.g., 1-3) revealed significant differences between the set and the actual temperature. These differences increased with decreasing temperature as shown in fig. 1.

At each temperature the NMR thermometer samples and the probe were allowed to equilibrate for more than 10 min in the absence of any irradiating field. A cross check of the accuracy of the thermocouple using ice and boiling water revealed that the thermocouple was functioning correctly. Thus the only remaining possibility for the error was improper sensing by the thermocouple. However, the thermocouple was inserted as far as possible into the probe (i.e., without inhibiting sample spinning). Thus, the thermocouple was positioned as close to the sample as the probe design would allow.

Although it is reasonable to expect that with modern spectrometers the set temperature should be close to the actual temperature experienced by the sample, this was not so in our case and we must rely on a calibration chart as shown in the figure to obtain accurate temperature control.

The moral of the story is don't trust a meter just because it claims that the temperature is accurate to 1 decimal place !

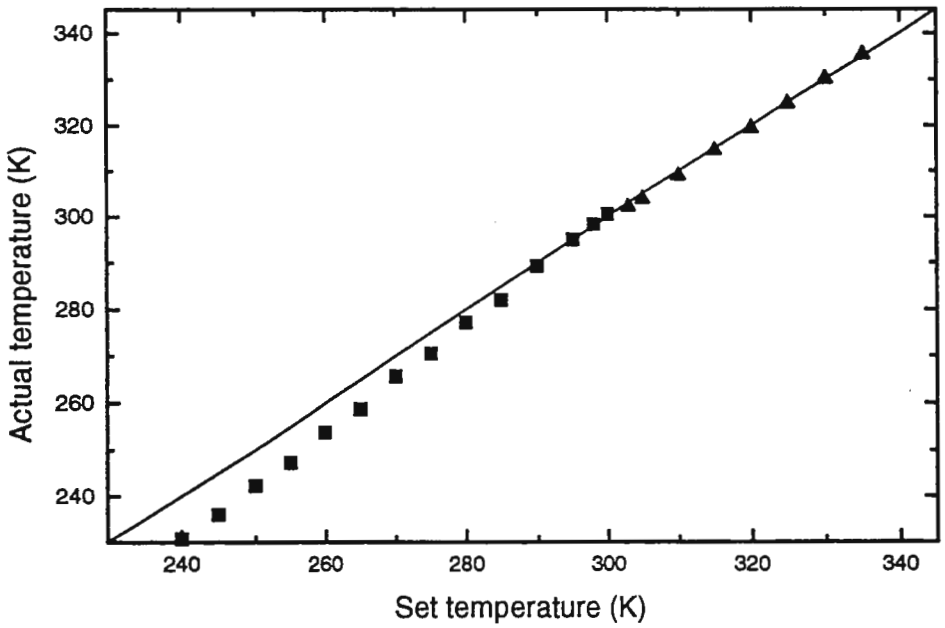

Fig. 1. Set versus actual temperature in the NMR probe. The triangles and squares denote temperatures calibrated using the ethylene glycol and methanol NMR thermometers, respectively. The solid line represents the ideal curve where there is exact correspondence between the set and actual temperatures.

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2) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227-2229.
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Please credit this to the account of Y. Arata.

Yours sincerely

W. S. Price

William S. Price

The NMR Revolution advances...

BRUKER

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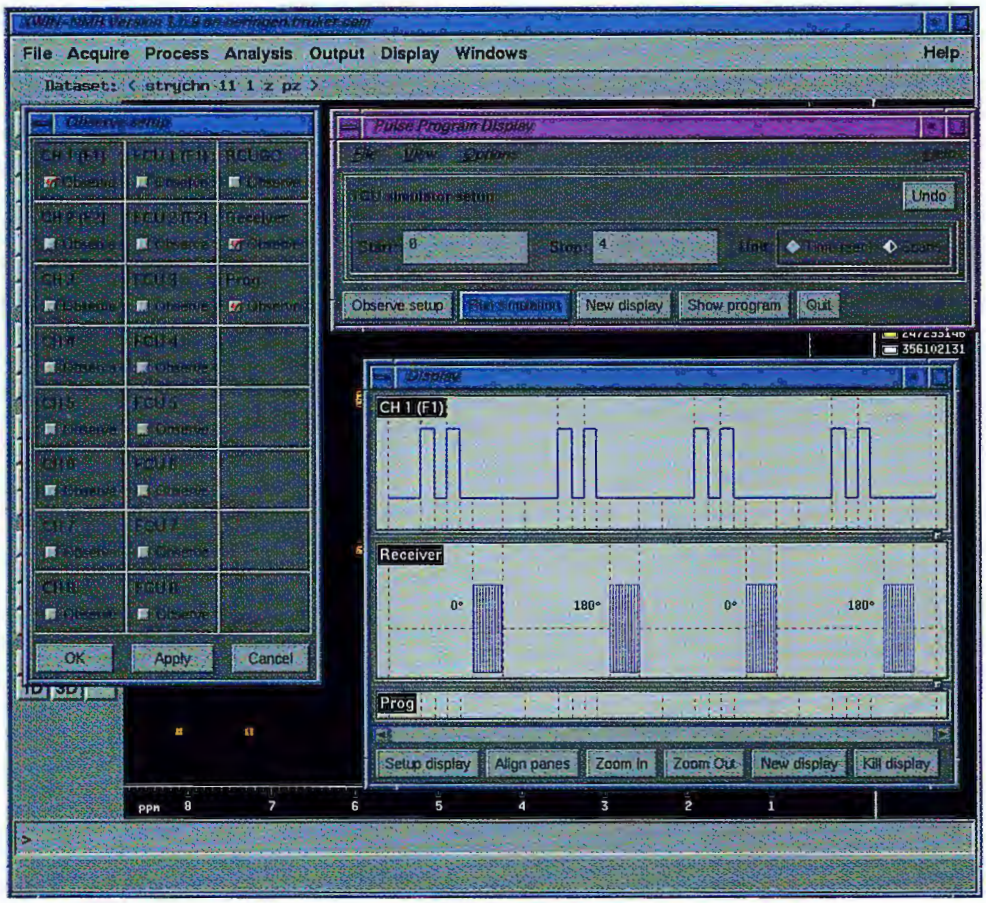
Pulse Program Display



The *Pulse Program Display* module in XWIN-NMR, Bruker's new NMR software package, provides **exact** graphical visualization of a pulse sequence on the *AVANCE* spectrometers. This includes illustration of the amplitude, timing and phase for all RF and gradient channels. All this to make even the most complicated experiment look easy!

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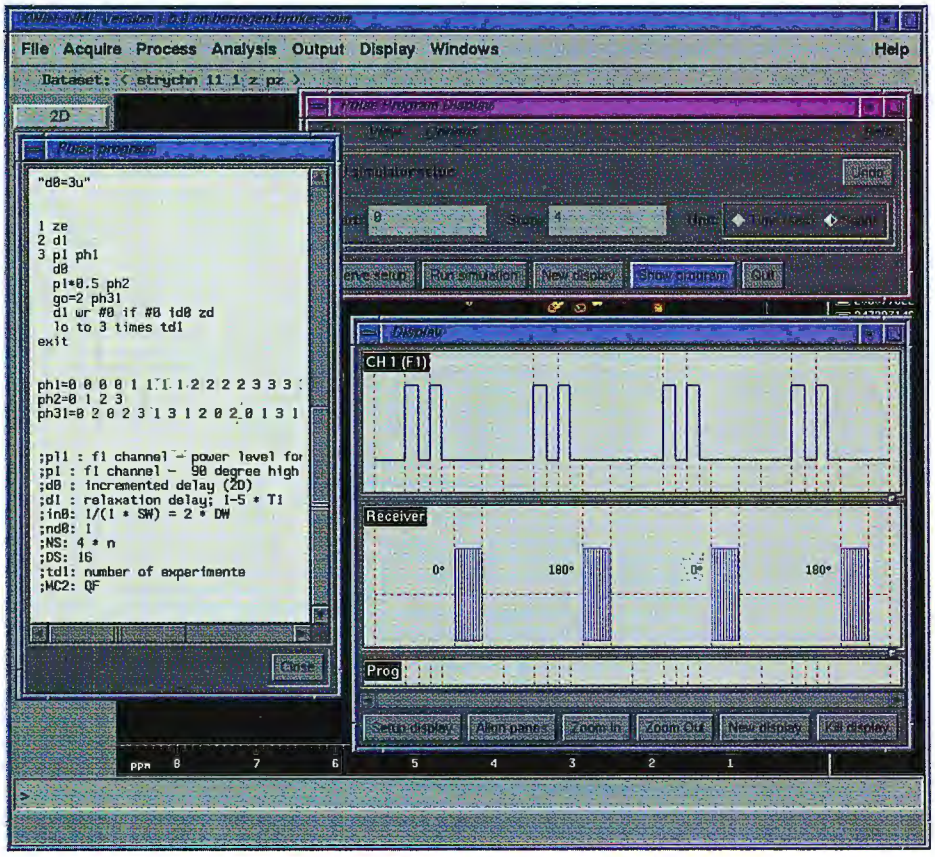

For more information on *Pulse Program Display* as well as XWIN-NMR, contact your local sales representative.

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30.04.1996

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(received 5/8/96)

Prof. Dr. B. L. Shapiro
The NMR Newsletter
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Palo Alto, CAL. 94303
USA

Working on the Structure of the *Transcarboxylase* Carrier

Dear Barry,

Getting on in age every nmr spectroscopist will perhaps end up in doing some protein work, since this seems to be currently the predominant application of our technique. We were interested in the action of biotin in enzymes [1] and have recently been able to detect a $^{15}N,^{13}C$ spin coupling constant of the unstable intermediate carboxybiotin during an enzymatic decarboxylation [2]. During this project we wanted to determine the structure of the biotin carrier of the *transcarboxylase*. However, due to aggregation this protein did not give acceptable nmr spectra. Together with K. H. Röhm we succeeded in preparing a deletion mutant, as shown below, which was fully labelled with ^{15}N. Here we communicate a rather nice looking H,N correlation (AMX-500) and we hope to get soon structural insights from 3D 600 MHz spectra obtained by T. Domke in Braunschweig.

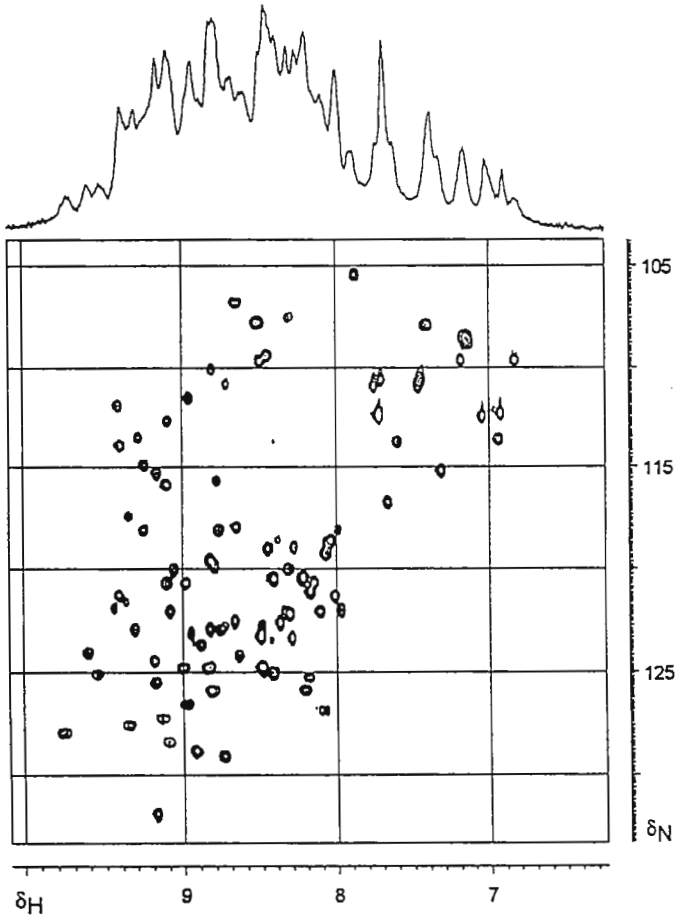
```
1              11              21              31              41
MKLKVTVNGTAYDVDVDVDKSHENPMGTILFGGGTGGAPAPRAAGGAGAGK
MKLKVTVNG.....................................................AGK
1                                                              11

51          61              71              81
AGEGEIPAPLAGTVSKILV KEGDTVKAGQ TVLVLEAMKM
AGEGEIPAPLAGTVSKILV KEGDTVKAGQ TVLVLEAMKM
            22              32              42

91             101             111             121
ETEINAPTDG KVEKVLVKER DAVQGGQGLI KIG
ETEINAPTDG KVEKVLVKER DAVQGGQGLI KIG
52             62              72              82
```

[S. Berger] [S. Bokorny] [K.-H. Röhm]

[1] K. Bendrat, S. Berger, W. Buckel, W. A. Etzel und K.-H. Röhm, FEBS Letters, **277**, 156-158 (1990).
[2] S. Berger, A. Braune, W. Buckel, U. Härtel, M. L. Lee, submitted.



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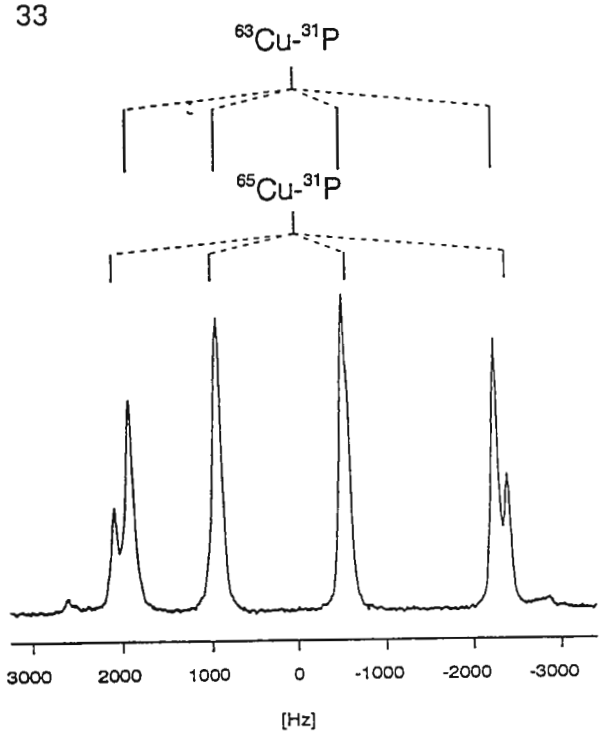

Figure 1: ^{31}P CP/MAS NMR spectrum of $Cu(PPh_3)_2NO_3$

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29 April 1996
(received 5/8/96)

Professor Bernard L. Shapiro
Editor/Publisher The NMR Newsletter
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Palo Alto, California
94303 USA

Phosphorus-Phosphorus Indirect Spin-Spin Coupling in Copper-Bisphosphines

Dear Barry:

The ^{31}P CP/MAS NMR spectrum of $Cu(PPh_3)_2NO_3$ is shown in Figure 1*. The unsymmetrical pattern due to $^{63/65}Cu$-^{31}P spin-spin coupling observed for this compound was first reported and interpreted by Menger and Veeman many years ago.[1] The observation of a single phosphorus site is consistent with the known crystal structure of this complex which indicates that the two phosphine ligands are related by a C_2 axis of symmetry which bisects the P-Cu-P angle.[2] The two ^{31}P nuclei are thus crystallographically equivalent but magnetically nonequivalent since they are not related by an inversion center.[3]

Magnetic nonequivalence of the two phosphorus sites of $Cu(PPh_3)_2NO_3$ becomes apparent when ^{31}P NMR spectra are acquired under conditions of slow magic angle sample spinning (e.g., 1 to 2 kHz). In this case, we observe extensive line broadening of all peaks, including the spinning sidebands due to $^2J(^{31}P,^{31}P)$. Although we have been unable to resolve this coupling in 1D spectra, application of the 2D *J*-resolved experiment clearly indicates that $|^2J(^{31}P,^{31}P)| = 157 \pm 5$ Hz. This is one of many systems that we have encountered where two phosphorus nuclei are crystallographically equivalent but magnetically nonequivalent.[4]

Anyone interested in further details can contact me via E-mail at RODW@IS.DAL.CA. Our research on the copper phosphines has been carried out by Gang Wu, Michael D. Lumsden, Klaus Eichele and Robert Schurko. Best regards.

*on page 32

Yours sincerely,

Rod

Roderick E. Wasylishen

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May 9th 1996

(received 5/21/96)

1D HETERO NOE EXPERIMENT ON A BRUKER DRX SPECTROMETER

Dear Dr. Shapiro

heteronuclear NOE experiments have turned out to be most valuable for assigning quaternery carbons and for unravelling unknown structures of molecules. If only one or a few such heteronuclear interactions are of interest the 1D version - offering the highest sensitivity - is probably the best choice. To obtain corresponding 1D difference spectra of highest quality several conditions must be fulfilled, one of which concerns the decoupler frequency for broadband decoupling during data acquisition, which should be the same throughout for all the individual sub-experiments. We designed a pulse program for our BRUKER DRX 500 spectrometer which takes advantage of a third channel and which circumvents the otherwise time-consuming setup of adequate frequency lists.
This third channel (f3) is used for broadband {1H} decoupling with the offset frequency O3 set to the center of the proton spectrum. The second channel (f2) is used to selectively irradiate the target protons with the offset frequency O2 taken from the freqency list. This frequency list looks the same as for a homonuclear NOE experiment and includes besides the offset frequencies for the selected protons at least one frequency set off-resonance to any proton signal.

```
;xnodiff.bi
;1D HETERO-NOE difference experiment
;avance-version

#include <Avance.incl>

d11 pl1:f1              ;d11     :30 ms for disk i/o
                        ;pl1     :power level for hard pulse (-6 dB)
d11 pl12:f3             ;pl12    :power level for cpd decoupling
d11 pl14:f2             ;pl14    :power level for cw/hd

1 ze
  d11 fq2:f2            ;fq2     :create list fq2list with menu option calib; store as f1 list
                        ;         off-resonance frequency should be at the end of the list
  d11 do:f2 do:f3
2 d1 do:f3              ;d1      :relaxation delay
  d20 cw:f2             ;d20     :irradiation time
  d13 do:f2             ;d13     : >= 10 ms
  p1:f1 ph1             ;p1      :hard pulse power level pl1
  go=2 ph31 cpd2:f3
  d1 wr #0 if #0
10 lo to 1 times td1    ;td1     :number of entries in frequency list
  d11 rf #0             ;parmod :2D!!!
  lo to 1 times l1      ;l1      :number of overall loops; total number of scans =l1*ns
  d11
13 exit

ph1=0 2 1 3
ph31=0 2 1 3
```

Yours sincerely

Peter Bigler
e-mail:bigler@ioc.unibe.ch

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81-000-11-9	1% $^{13}CH_3I$/1% Trimethyl Phosphite/0.2% $Cr(AcAc)_3$	5mm x 8"	99; 99.96
82-001-62-9	1% Chloroform/Acetone-d_6	2.5mm x 5mm x 8"	99.9%
82-001-17-3	1% Chloroform/Acetone-d_6	3mm x 8"	99.9%
82-001-03-3	1% Chloroform/Acetone-d_6	5mm x 8"	99.9%
82-009-08-5	1% Chloroform/Acetone-d_6	8mm x 7"	99.9%
82-001-60-3	1% Chloroform/Acetone-d_6	8mm x 8"	99.9%
82-001-12-4	1% Chloroform/Acetone-d_6	10mm x 8"	99.9%
82-001-99-1	1% Chloroform/$CDCl_3$	3mm x 8"	99.8%
82-001-98-3	1% Chloroform/$CDCl_3$	5mm x 8"	99.96%
82-001-18-1	5% Chloroform/Acetone-d_6	3mm x 8"	99.9%
82-001-45-4	5% Chloroform/Acetone-d_6	4mm nanotube	99.9%
82-009-09-3	5% Chloroform/Acetone-d_6	2.5mm x 5mm x 7"	99.9%
82-001-14-0	5% Chloroform/Acetone-d_6	5mm x 8"	99.9%
82-001-49-6	20% Chloroform/Acetone-d_6	5mm x 8"	99.9%
82-001-85-0	50% $CDCl_3$/50% TMS	5mm x 8"	99.8%
82-001-52-0	20% 2,3-Dibromopropionic Acid/2% TMS/Benzene-d_6	5mm x 7"	99.6%
82-001-10-8	1% 1,2-Dichlorobenzene/Acetone-d_6	2.5mm x 5mm x 8"	99.9%
82-009-12-7	1% 1,2-Dichlorobenzene/Acetone-d_6	3mm x 8"	99.9%
82-001-00-9	1% 1,2-Dichlorobenzene/Acetone-d_6	5mm x 8"	99.9%
82-009-14-3	5% 1,2-Dichlorobenzene/Acetone-d_6	5mm x 8"	99.9%
82-009-10-1	0.1% Ethylbenzene/0.01% TMS/0.1mg/ml $Cr(AcAc)_3$/$CDCl_3$	5mm x 8"	99.8%
82-001-16-5	0.1% Ethylbenzene/0.01% TMS/$CDCl_3$	3mm x 8"	99.8%
82-001-42-1	0.1% Ethylbenzene/0.01% TMS/$CDCl_3$	4mm nanotube	99.8%
82-001-61-1	0.1% Ethylbenzene/0.01% TMS/$CDCl_3$	2.5mm x 5mm 8"	99.8%
82-000-93-6	0.1% Ethylbenzene/0.01% TMS/$CDCl_3$	5mm x 8"	99.8%
82-001-58-7	0.1% Ethylbenzene/0.01% TMS/$CDCl_3$	8mm x 8"	99.8%
82-001-86-8	0.1% Ethylbenzene/0.01% TMS/$CDCl_3$	10mm x 8"	99.8%
82-009-07-7	0.1% Ethylbenzene/$CDCl_3$	8mm x 7"	99.8%
82-001-53-8	5% Formamide/DMSO-d_6	5mm x 8"	99.9%

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CATALOG #	DESCRIPTION	TUBE	ENRICHMENT
82-001-92-6	0.1mg/ml $GdCl_3/D_2O$	10mm x 8"	99.9%
82-001-43-9	0.1mg/ml $GdCl_3/D_2O$	4mm nanotube	99.9%
82-001-90-0	0.1mg/ml $GdCl_3$/0.1% DSS/1% H_2O/D_2O	3mm x 8"	99.9%
82-001-47-0	0.1mg/ml $GdCl_3$/0.1% DSS/1% H_2O/D_2O	5mm x 8"	99.9%
82-001-59-5	0.1mg/ml $GdCl_3$/0.1% DSS/1% H_2O/D_2O	8mm x 8"	99.9%
82-001-15-7	0.2mg/ml $GdCl_3$/0.1% DSS/1% H_2O/D_2O	5mm x 8"	99.9%
82-001-56-1	25% Hexamethyldisiloxane/Benzene-d_6	5mm x 8"	99.6%
82-001-73-6	2mg/ml Nicotine/0.05% TMS/Acetone-d_6	5mm x 8"	99.9%
82-001-74-4	2mg/ml Nicotine/0.05% TMS/Acetonitrile-d_3	5mm x 8"	99.8%
82-001-70-2	2mg/ml Nicotine/0.05% TMS/Benzene-d_6	5mm x 8"	99.6%
82-001-72-8	2mg/ml Nicotine/0.05% TMS/DMSO-d_6	5mm x 8"	99.9%
82-001-75-1	2mg/ml Nicotine/0.05% TMS/Methanol-d_4	5mm x 8"	99.8%
82-001-89-2	40% P-Dioxane/5mg/ml $Cr(AcAc)_3$/Benzene-d_6	3mm x 8"	99.6%
82-001-44-7	40% P-Dioxane/5mg/ml $Cr(AcAc)_3$/Benzene-d_6	4mm nanotube	99.6%
82-001-54-6	40% P-Dioxane/5mg/ml $Cr(AcAc)_3$/Benzene-d_6	5mm x 8"	99.6%
82-001-46-2	40% P-Dioxane/5mg/ml $Cr(AcAc)_3$/Benzene-d_6	10mm x 8"	99.6%
82-001-93-4	40% P-Dioxane/Benzene-d_6	3mm x 8"	99.6%
82-001-41-3	40% P-Dioxane/Benzene-d_6	4mm nanotube	99.6%
82-001-63-7	40% P-Dioxane/Benzene-d_6	2.5mm x 5mm x 8"	99.6%
82-001-48-8	40% P-Dioxane/Benzene-d_6	5mm x 8"	99.9%
82-001-94-2	40% P-Dioxane/Benzene-d_6	5mm x 8"	99.6%
82-001-97-5	85% Phosphoric Acid(W/V)/D_2O	5mm x 8"	99.9%
82-001-68-6	85% Polyphosphoric Acid/D_2O	5mm x 8"	99.9%
82-001-55-3	0.2M Potassium Fluoride/10% D_2O/90% H_2O	10mm x 8"	99.9%
82-001-69-4	2mg/ml Sucrose/0.75% TSP/D_2O	5mm x 8"	99.9%
82-001-01-7	0.05% Trifluorotoluene/Benzene-d_6	5mm x 8"	99.6%
82-001-67-8	5% Trimethlyphosphite/$CDCl_3$	5mm x 8"	99.8%
82-001-95-9	0.0485M Triphenyl Phosphate/$CDCl_3$	3mm x 8"	99.8%
82-001-02-5	0.0485M Triphenyl Phosphate/$CDCl_3$	5mm x 8"	99.8%
82-001-11-6	0.0485M Triphenyl Phosphate/$CDCl_3$	10mm x 8"	99.8%
81-000-13-5	20mg/ml Urea^{13}C,$^{15}N_2$/DMSO-d_6	2.5mm x 5mm x 8"	99;99;99.9%
81-000-14-3	20mg/ml Urea^{13}C,$^{15}N_2$/DMSO-d_6	5mm x 7"	99;99;99.9%
81-000-12-7	20mg/ml Urea^{13}C,$^{15}N_2$/DMSO-d_6	8mm x 7"	99;99;99.9%
81-000-15-0	1M Urea-$^{15}N_2$/DMSO-d_6	5mm x 8"	99;99.9%

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April 24, 1996
(received 5/3/96)

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

Dear Barry,

In October of last year we travelled to the Antarctic to conduct NMR studies of the material properties of Antarctic sea ice. Sea ice is a critical component of global climate models, due to it's large albedo and influence on heat transport from the oceans to the atmosphere. Increased understanding of sea ice structure, and hence transport properties, will allow for refinement of such models. The Antarctic research (Oct. 24-Nov. 17, 1995 New Zealand Antarctic Programme Event K131) utilises and includes further development of an Earth's Field NMR apparatus which operates in the earth's magnetic field, as opposed to strong magnetic fields induced in laboratory settings by superconducting magnets. It is a robust and relatively inexpensive apparatus with potential for on site environmental and geophysical applications.

A scientific expedition to the Antarctic begins in Christchurch New Zealand. There you are outfitted with survival clothing including oversize mukluk boots that any circus clown would be proud of. After outfitting a last evening of civilisation in Christchurch can be enjoyed. Ours consisted of dinner and a lively Irish band and the requisite Irish brew. The morning of departure begins with a 5 am pickup and transport to the International Antarctic Centre where formal customs procedures are carried out. We boarded our US Air Force C141 Starlifter at about 9 am. At 11 am we were informed that the weather at McMurdo Sound was too bad for landing so the mission was scrubbed. The pleasure of two hours in survival gear strapped into a canvas belt seat on a Tarmac in 15C weather cannot be fully appreciated unless one has been there. The following day we fared better and our flight departed. Stepping off the plane onto the ice runway the sense of being on another planet was overwhelming. The air was crystal clear, temperature -21C, and the mountains hundreds of kilometres distant looked as if one could touch them.

The next three days at Scott Base were extremely busy. The first order of business was making sure all the scientific gear had arrived and being briefed on NZAP procedures. The next day was Antarctic Field Training , including crevasse safety, ice climbing and construction of and an overnight in a snow shelter. After AFT was the sorting out of tents, food and other gear for our three weeks living on the ice and testing of the NMR apparatus. A filter was inoperative and a new one was built at Scott Base using components we had brought with us. We departed for our field camp in a convoy led by several snowmobiles we would use for transport at the camp. These were followed by a Hagglunds tracked vehicle and the bulldozer from McMurdo Base which towed the gear and several box car style containers, including a 20kW generator for our field lab and camp.

Our field camp was located 2 kms off Cape Evans, the site of Scott's 1910-1911 hut from the Terra Nova Expedition, in McMurdo Sound. The camp was on 2m of sea ice over 300m of ocean. The weather was perfect for setting up, still and relatively warm, -15C. After assembling and anchoring all the shelters to the ice we immediately set up

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Fig. 1 K131 field camp with Mt. erebus in the background and distinguished visitors foreground.

the EFNMR apparatus and began tests of free induction decay and spin echo experiments on unfrozen water and ethanol samples in the 65μT earth's magnetic field. With the apparatus functioning well and calibration measurements of signal intensity, T_2 relaxation and diffusion made we were ready to obtain ice cores. After about a day of working on ice cores a blizzard with winds in excess of 100 km/h struck and kept us in our tents for five days. This was followed by five clear days during which the majority of our measurements were made by working in 24 hour shifts. Our return to Scott Base was delayed by another blizzard, but ourselves, our equipment and our data all returned safely.

Doing NMR under the extreme conditions of the Antarctic is an adventure like no other. The historical context of the pursuit of science in a place with a rich tradition exemplified by men like Robert Falcon Scott, who gave his life for science by not abandoning his scientific samples, is an aspect of the work which is most gratifying.

Sincerely,

Joseph D. Seymour Paul T. Callaghan Craig D. Eccles

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– *the natural fit for deuterated NMR solvents*

Aldrich offers all major deuterated NMR solvents in 100mL Sure/Seal bottles. This packaging option has quickly become popular because it minimizes both moisture contamination and the loss of TMS during transport and storage.

Until recently, NMR solvents were dispensed from Sure/Seal bottles by using either a syringe-needle technique or a traditional pipetting technique, which limited the utility of this unit. Chemists in the high-field NMR laboratory at Aldrich found the new OPTIFIX dispensers (purchased separately) to be ideal for accurate and reproducible dispensing of variable volumes of deuterated NMR solvents such as chloroform-*d*, methanol-d_4, DMSO-d_6, and acetone-d_6.

OPTIFIX is an inert dispenser system that provides:

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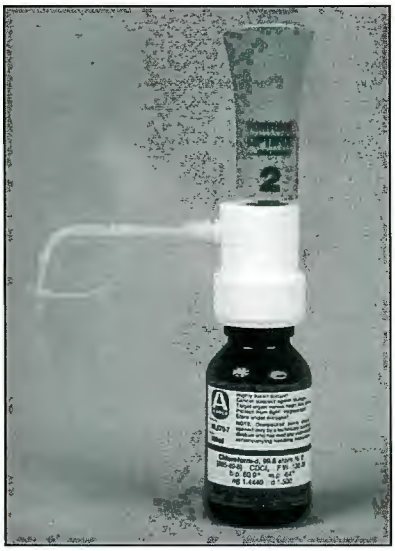
- Easily adjustable to dispense different volumes. Simply adjust a knurled screw and lock nut.

The Sure/Seal-OPTIFIX system, along with our single-use ampules (0.5, 0.75, and 1.0mL) for deuterated NMR solvents, eliminate the need for using other systems/packaging, yet continue to provide you the flexibility of choosing the volume that best fits your needs.

So, the next time you are ordering an NMR solvent, why not consider the Aldrich Sure/Seal-OPTIFIX system? You may never go back to traditional systems!



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43,875-8	**Acetone-d_6**, 99.8 atom % D	**100mL**	**$147.50**
43,873-1	**Acetone-d_6**, 99.5 atom % D	**100mL**	**$141.50**
43,869-3	**Acetonitrile-d_3**, 99.6 atom % D	**100mL**	**$205.00**
43,868-5	**Benzene-d_6**, 99.6 atom % D	**100mL**	**$174.50**
43,870-7	**Chloroform-*d***, 99.8 atom % D	**100mL**	**$39.00**
15,182-3	**Chloroform-*d***, 99.8 atom % D	**125g**	**$32.50**
43,872-3	**Chloroform-*d***, 99.8 atom % D (contains 0.03% v/v TMS)	**100mL**	**$39.00**
43,871-5	**Chloroform-*d***, 99.8 atom % D (contains 1% v/v TMS)	**100mL**	**$39.00**
22,578-9	**Chloroform-*d***, 99.8 atom % D (contains 0.03% v/v TMS)	**125g**	**$32.50**
15,183-1	**Chloroform-*d***, 99.8 atom % D (contains 1% v/v TMS)	**125g**	**$32.50**
43,876-6	**Deuterium oxide**, 100.0 atom % D	**100g**	**$151.50**
43,877-4	**Deuterium oxide**, 99.9 atom % D	**100g**	**$57.50**
43,867-7	**Methyl-d_3 alcohol-*d***, 99.8 atom % D	**100mL**	**$398.50**
45,052-9	**Methyl sulfoxide-d_6**, 99.5+ atom % D	**100mL**	**$157.00**

OPTIFIX Dispensers

Dispenser Model	Piston Type	Features
BASIC	PTFE-encased glass	Has glass dispensing barrel.
SOLVENTS	Glass	Has safety-coated glass dispensing barrel.

Range (mL)	Increment (mL)	BASIC MODEL Cat. No.	SOLVENTS MODEL Cat. No.	Each
0.2-1.0	0.05	**Z25,998-5**	—	$251.00
0.4-2.0	0.1	**Z25,999-3**	**Z26,009-6***	251.00
1.0-5.0	0.1	**Z26,000-2**	**Z26,011-8**	251.00
2.0-10.0	0.2	**Z26,001-0**	**Z26,012-6**	251.00

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New Products for NMR

Chemists in the Stable Isotopes group at Aldrich are committed to serving the product needs of our customers in the fields of NMR spectroscopy. We are continually expanding this product line to ensure that NMR researchers will have to look no further than the Aldrich Stable Isotopes Catalog to find what they need. Below are a few examples of products we have added for customers involved in NMR-related research.

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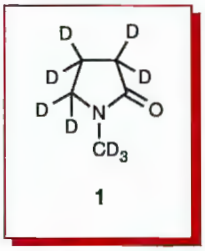
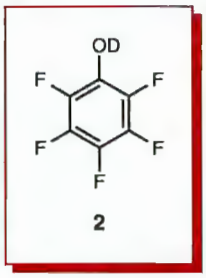


1

44,813-3 **1-(Methyl-d_3)-2-pyrrolidinone-d_6**, 99 atom % D **(1)**
1g $130.00; 5g $470.00

39,430-0 **Trifluoroacetic acid-*d***, 99 atom % D
10mL $28.00; 50mL $120.00

36,963-2 **Trifluoromethanesulfonic acid-*d***, 98 atom % D
1g $15.40; 5g $51.50; 10g $85.40



2

41,195-7 **Pentafluorophenol-*d***, 99 atom % D **(2)**
1g $41.50; 5g $138.50

35,870-3 **1,1,2,2-Tetrachloroethane-d_2**, 99.5+ atom % D
1g $14.90; 5g $49.40; 25g $165.00

39,289-8 **2-Propanol-*1,1,1,3,3,3*-d_6**, 99 atom % D
1g $55.10; 5g $183.60

42,536-2 **1,2-Dibromoethane-d_4**, 99 atom % D
5g $60.00; 25g $200.00

TMS/TSP listings

43,487-6 **Chloroform-*d***, 99.8 atom % D (contains 0.1% v/v TMS) **100g $23.30; 125g $32.50; 500g $96.30; 10 x 100g $181.00; 50 x 100g $710.00**

45,051-0 **Deuterium oxide,** 99.9 atom % D (contains 0.05 wt. % TSP-d_4) **25mL $23.50; 100mL $64.50; 10 x 100mL $569.50**

43,902-9 **Methyl-d_3 alcohol-*d***, 99.8 atom % D (contains 0.1% v/v TMS)
5g $35.00; 10g $57.95; 50g $248.85

43,903-7 **(Methyl sulfoxide)-d_6**, 99.9 atom % D (contains 0.1% v/v TMS)
10g $17.35; 25g $40.70; 50g $78.15; 10 x 10g $144.50

Solvents in 0.75mL single-use ampules (1pkg = 10 x 0.75mL)

44,476-6 **(Methyl sulfoxide)-d_6**, 100.0 atom % D
0.5pkg $51.00; 1pkg $85.00; 5 x 1pkg $375.00

44,139-2 **(Methyl sulfoxide)-d_6**, 99.9 atom % D
0.5pkg $10.00; 1pkg $16.50; 5 x 1pkg $78.00

44,138-4 **Methyl-d_3 alcohol-*d***, 99.8 atom % D
0.5pkg $26.50; 1pkg $44.00; 5 x 1pkg $160.00

44,137-6 **Deuterium oxide,** 99.9 atom % D
0.5pkg $8.50; 1pkg $12.50; 5 x 1pkg $48.00

44,473-1 **Chloroform-*d***, 100.0 atom % D
0.5pkg $16.00; 1pkg $28.00; 5 x 1pkg $120.00

NOTE: Other solvents/purities are available in 0.75 single-use ampules. Please refer to the 1996 Stable Isotopes Catalog for details.

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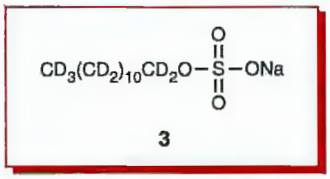
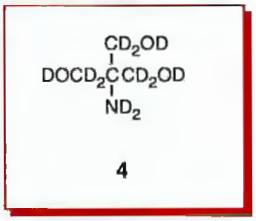


3

45,185-1 **Dodecyl-d_{25} sulfate, sodium salt (3)**
100mg $53.50; 500mg $195.00

44,910-5 **Tris(hydroxymethyl-d_3)amino-d_2-methane,** 98 atom % D **(4)** **1g $148.50**



4

45,184-3 **Dithiothreitol-d_{10},** 98 atom % D
100mg $250.00; 250mg $495.00

43,729-8 **Imidazole-d_4,** 98 atom % D
250mg $72.00; 1g $200.00

44,048-5 **Ammonium-d_4 acetate-d_3**, 98 atom % D
1g $33.50; 5g $112.50

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

May 23, 1996
(received 5/24/96)

MAGNETIZATION-TRANSFER NMR ANALYSIS OF AQUEOUS POLY(VINYL ALCOHOL) GELS: EFFECT OF HYDROLYSIS AND AGE ON NETWORK FORMATION

Dear Dr. Shapiro:

We are using magnetization-transfer (MT) NMR to probe network formation in aqueous poly (vinyl alcohol) (PVA) gels. The MT data is evaluated by the curve-fitting method originally described by Eads and Wu (*Carbohydrate Polymers* 20 **1993**, 51-60; *J. Agric. Food Chem.* 40 **1992**, 449-455). This method allows us to analyze the MT profiles as a sum of a Gaussian component, characteristic of the rigid component of the gel and a Lorentzian component characteristic of the liquid-like component in the gel. Evaluation of the Gaussian component will be used to make correlations to physical properties of aqueous gels such as rigidity and crystallinity.

First, we would like to mention some of the difficulties encountered with analyzing samples with high water concentrations. Our MT profiles are acquired on an AMX 360 by a series of presaturation experiments with the offset varied between +50 and -50 kHz. Full saturation is achieved with a 3 second presaturation pulse at a rf field of 500 Hz. Due to the viscosity of our samples we are constrained to use 10 mm NMR tubes. MT profiles acquired in 10 mm NMR tubes with a 10 mm insert contained scatter. Heating and radiation damping were suspect. Randomizing the frequency-offsets in the variable delay list instead of systematically saturating from negative offsets to zero to positive offsets was successful; the scatter was reduced and no longer pronounced on the positive side of the MT profile. Radiation damping was minimized by using a 25 mm insert. The result, smooth MT profiles even at greater than 95% water concentrations.

Thus far, we have evaluated network formation in aqueous PVA gels by MT analysis as a function of polymer concentration, degree of hydrolysis and age of the gel. The total area of the MT profile increases with polymer concentration (Figure). The total area of the MT profiles should be directly related to the amount of polymer in the system and increase linearly with PVA concentration. Our results show a nonlinear increase in profile area with increasing PVA concentration. This nonlinearity is due to an increase in gel rigidity promoted by network formation. These results reveal that network formation in aqueous PVA gels is more pronounced at higher concentrations. The degree of network formation is also sensitive to the degree of hydrolysis of the PVA. For samples with PVA concentrations >20%, the hydrogen-bonding between hydroxyl groups responsible for promoting network formation is hindered by 3% vinyl acetate.

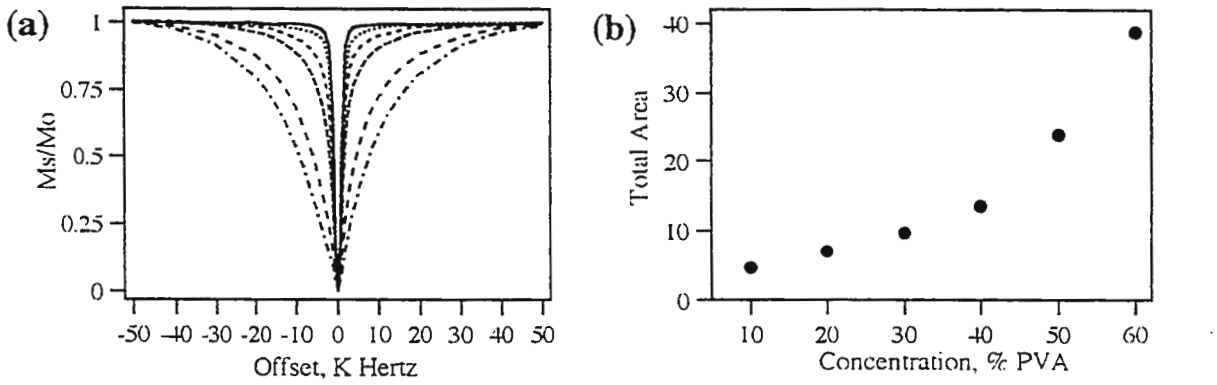
MT analysis is also sensitive to changes in the degree of network formation as a result of polymer prehistory, dissolution conditions, additives and storage temperature. This study has shown that MT analysis can be extended to the analysis of network formation in physically cross-linked

aqueous gels in addition to previously highly ordered chemically cross-linked gels.

Subsequent experiments will involve correlating the area of the Gaussian component to physical properties of gels such as rigidity, viscosity and crystallinity by rheometry and Raman spectroscopy. Our overlying goal is to use this PVA gel system as a means of establishing the NMR measurable parameters associated with the characterization of gels and the dynamic behavior that governs their physical and mechanical properties.

Sincerely,

Bill Anderson Lori Stephans D. J. Wang Natalie Foster Jim Roberts



(a) Offset-frequency dependence on the water magnetization as a function of polymer concentration via selective saturation. (b) Profile area as a function of PVA concentration.The PVA used in this analysis was 80% hydrolyzed and had a M_w of 10,000. (——) 10%, (·····)20%, (---·) 30%, (----) 40%, (- - -) 50% and (---·) 60% PVA/water by weight.

Notice:

Subscription renewal invoices for the October 1996 - September 1997 Newsletter year will be mailed on June 29, for receipt of payment by September 5, 1996. Prompt processing of your invoice will be greatly appreciated.

The subscription rate for the 1996-97 year has again been set at $190.00, with the usual 50% discount for academic or personal subscriptions. While there will be no increase in the subscription rate, a small increase in the optional Air Mail Printed Matter mailing charge for overseas subscribers is necessary.

B. L. Shapiro
1 June 1996

Address all Newsletter correspondence to:

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

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Deadline Dates

No. 454 (July)	28 June 1996
No. 455 (August)	26 July 1996
No. 456 (Sept.)	23 Aug. 1996
No. 457(Oct.)	27 Sept. 1996
No. 458 (Nov.)	25 Oct. 1996

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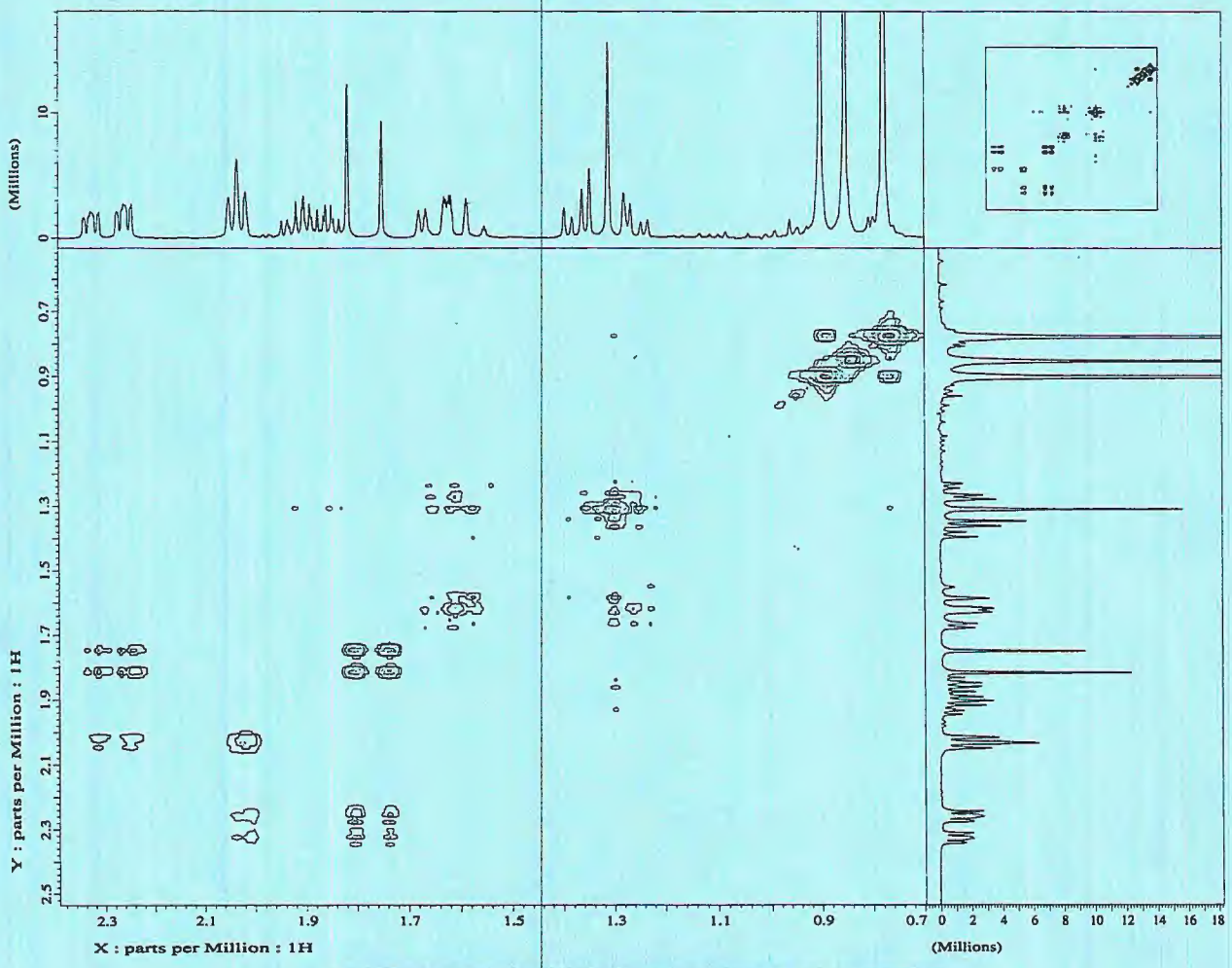

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