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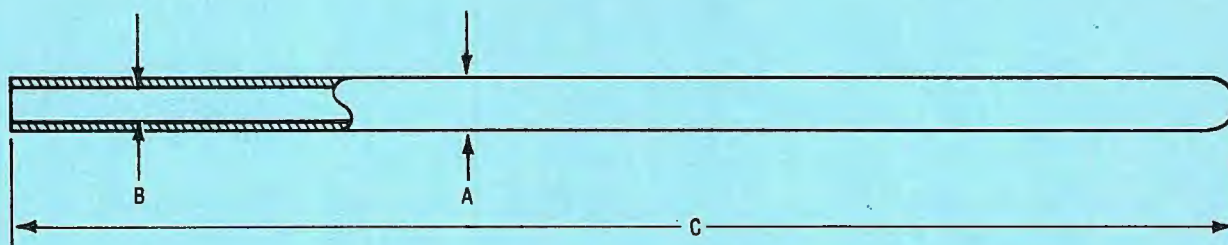
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## FORTHCOMING NMR MEETINGS

27th Annual Eastern Analytical Symposium and Exposition, October 2 - 7, 1988; New York Hilton Hotel, New York; General Chairman - Dr. Harvey S. Gold, Polymer Products Dept., E256/308, E. I. du Pont de Nemours & Co., Wilmington, DE 19898; (302) 695-3669.

International Post-Graduate Course 'NMR in Agriculture, Plants and Products', October 3 - 15, 1988; Wageningen, The Netherlands; Dr. Ir. J. H. de Ru, Foundation for Post-Graduate Courses, Agricultural University, Hollansegweg 1, NL-6706 KN Wageningen, The Netherlands.

Second Missouri Magnetic Resonance Symposium, October 25, 1988; St. Louis, Missouri; Contact Dr. D. W. Larsen (314) 553-5341 or Dr. F. D. Blum (314) 341-4451, Bitnet: C2828@UMRVMB.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence  
Should Be Addressed To:

Dr. Bernard L. Shapiro  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303, U.S.A.  
(415) 493-5971

## DEADLINE DATES

No. 362 (November)—21 October 1988  
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July 20, 1988  
(received 7/30/88)

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

 $^{13}\text{C}$  NMR Assignment of tetrahydrocarbazole and its 1-oxo analogue

Dear Professor Shapiro:

In a recent work Katritzky et al.<sup>1</sup> interchanged the C-6 and C-7 signals of tetrahydrocarbazole (1) from the original assignments done by Roberts<sup>2</sup>. For this purpose they used the 8-deutero analogue, although such a reassignment was already proposed in our review paper<sup>3</sup>. However the authors<sup>1</sup> were unable to assign the aliphatic carbon signals of 1.

On the other hand, in the same review<sup>3</sup> we reassigned the C-4a and C-4b signals of a series of alkaloids containing a carbonyl group at the C-1 position of tetrahydrocarbazole. This situation prompted Noland and Condoluci<sup>4</sup> to publish their speculations to again reverse our reassignments.

In order to definitively settle the two above mentioned compounds, we performed detailed  $^{13}\text{C}$  nmr measurements that undoubtedly allow to completely assign the spectra of tetrahydrocarbazole (1) and of 1-oxotetrahydrocarbazole (2) both in  $\text{CDCl}_3$  and in  $\text{DMSO}-d_6$  solutions.

The  $^1\text{H}$  and  $^{13}\text{C}$  signal assignments for the aromatic methine groups of 1 and 2 were deduced by the combined use of 2D  $^{13}\text{C}$ - $^1\text{H}$  correlated spectra and by standard  $^1\text{H}[^1\text{H}]$  decoupling experiments, as already detailed for indole<sup>5</sup>.

The resonances due to the aliphatic carbons of 1 were assigned from 2D HETCOR experiments and by analysis of the long-range isotope effects ( $n\Delta$ ), when the labil NH was partially exchanged to ND<sup>5,6</sup>. The C-1/C-4 pair (20.7, 22.8 ppm in  $\text{DMSO}-d_6$ ) is correlated to the downfield triplets in the  $^1\text{H}$  domain and thus allows to identify the C-2/C-3 pair (22.9, 23.1 ppm in  $\text{DMSO}-d_6$ ). Furthermore, the absorption at 23.1 ppm is not influenced by H/D exchange and is ascribed to C-3 ( $^5\Delta$ ), while the signal at 22.9 ppm is assigned to C-2 ( $^4\Delta_{\text{C-2}} = 8.9$  ppb). Similarly for the C-1/C-4 pair, the deuterium-induced shift for C-1 at 22.8 ppm is 39.8 ppb ( $^3\Delta$ ), and that of C-4 at 20.7 ppm is 7.2 ppb ( $^4\Delta$ ).

The aliphatic region of 2 is assigned from a 2D HETCOR experiment, since C-2 appears near 38.2 ppm. Selective proton decoupling experiments and analysis of the long-range isotope effects were carried out to support the assignments of the quaternary signals (C-4a, C-4b, C-8a and C-9a) of 1 and 2. The unambiguous distinction of the C-4a/C-4b pair in 2 was achieved by selective irradiation at the 2H-3 quintet. Thereby C-4a lost its  $^3J_{\text{CH}}$  coupling constants, while all the multiplicities of the remaining  $\text{sp}^2$  carbons, excepting the carbonyl group, stayed unaltered. Thus, C-4a appears at 129.7 ppm in  $\text{CDCl}_3$  and at 127.9 ppm in  $\text{DMSO}-d_6$ , in agreement with our re-assigned<sup>3</sup> shifts in the 128.8-126.7 ppm region for a series of alkaloids







State University of New York  
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Division of Radiological Sciences  
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July 26, 1988  
(received 8/1/88)

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

Magnetic Resonance Images -- Hardcopy via Laser Printer

Dear Barry:

A recent technical advance has been made in the hardcopy of MR images on a laser printer (Hewlett Packard LaserJet). The smallest dot our printer can make has no variation in intensity. However, since the printer can make 300 dots per inch, we can construct each pixel in the image from a square matrix of printer dots. The intensity of each pixel is determined by how many of these dot locations in a pixel are black. Various techniques have been evaluated for locating the dots within these pixels. A "herring-bone" artifact occurs when each pixel intensity corresponds to one unique dot pattern (Fig 1). More "photograph-like" results have been achieved by randomizing the location of the dots within each pixel (Fig. 2).

Besides being very convenient, a possible advantage over traditional grey scale is that reproduction of these Laser Printer images by Xerox or photography is less dependent on linearity or dynamic range of the reproduction technique (on the small scale each element is either "all white" or "all black").

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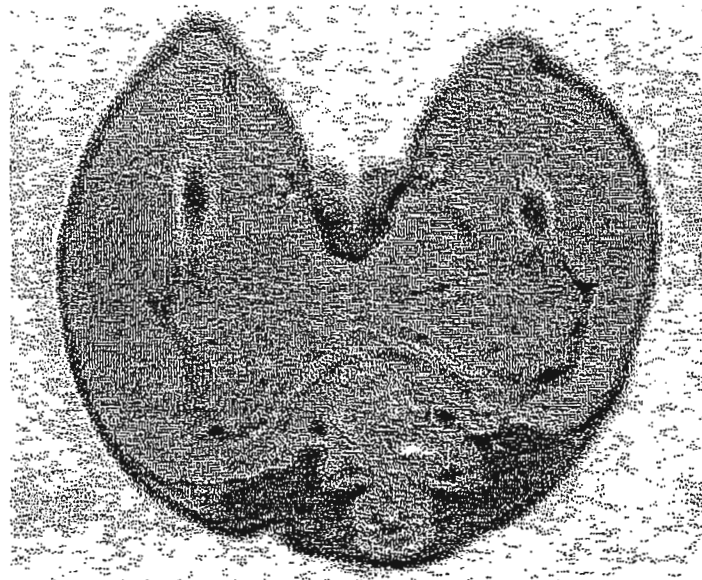


Fig. 1.

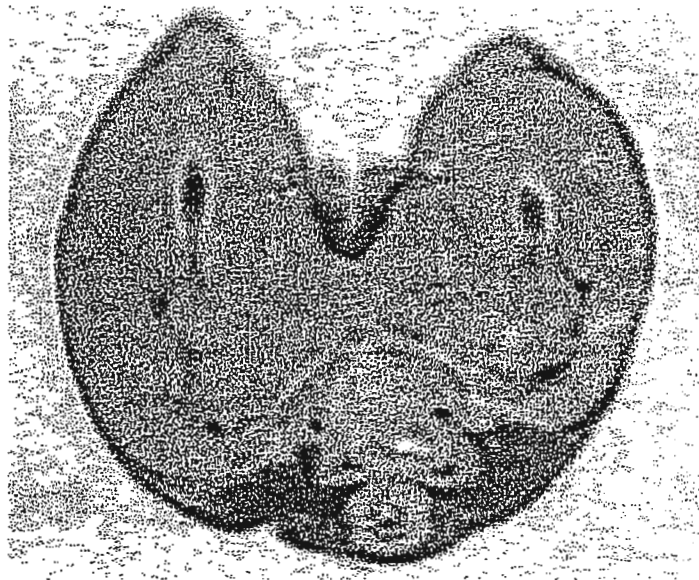


Fig. 2

Best regards:

*George Stetten*  
George Stetten

*Nick Szevenyi*  
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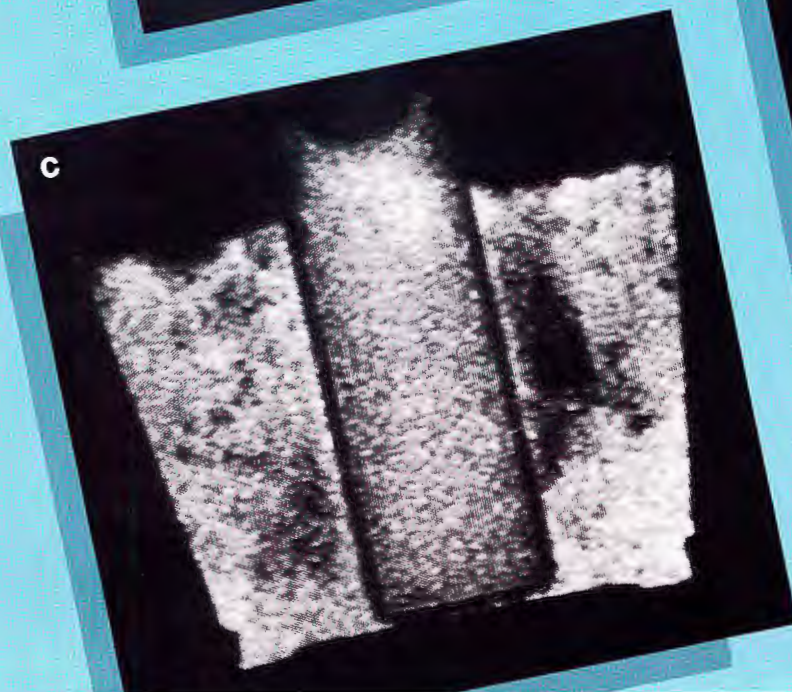
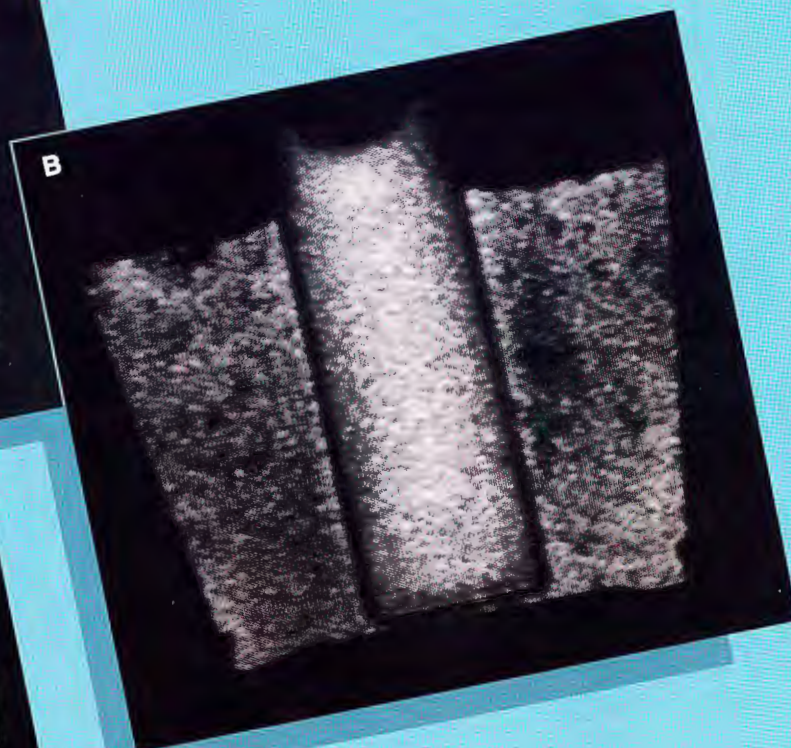
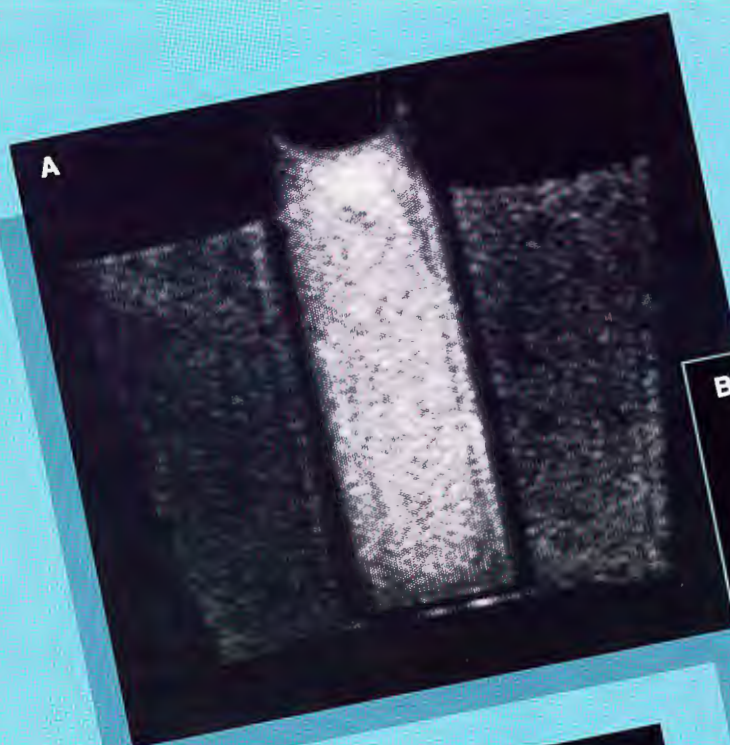
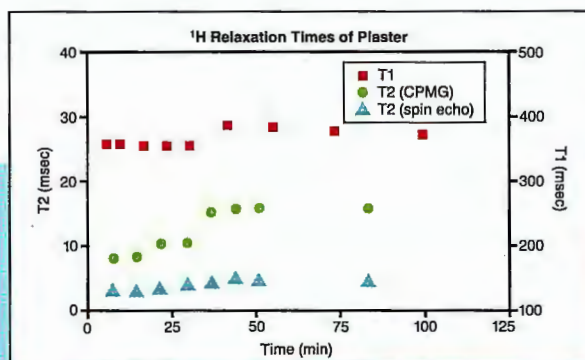
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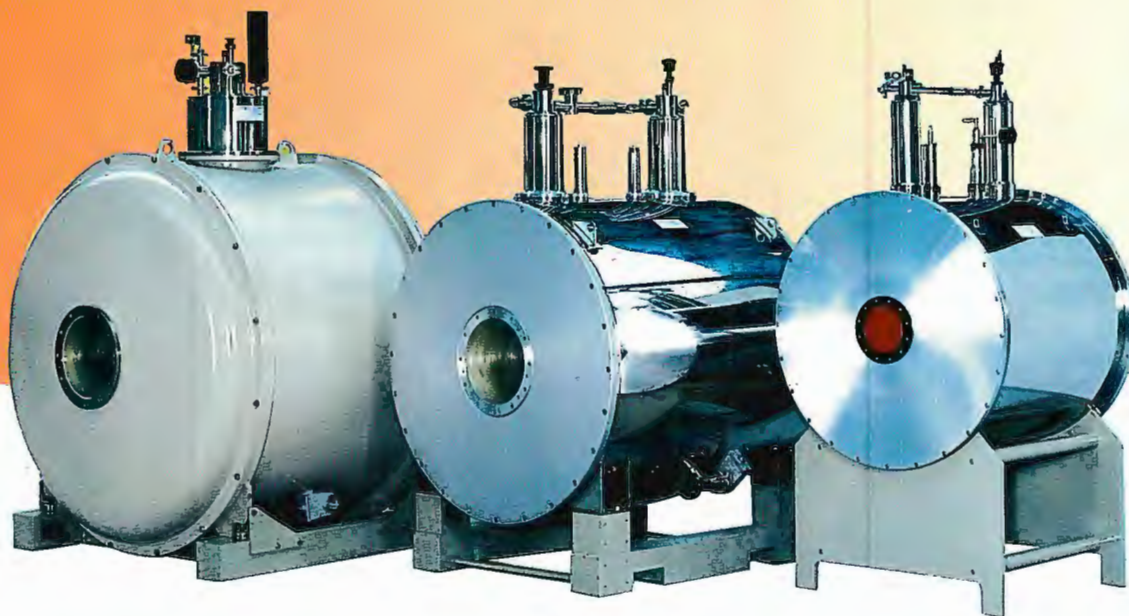
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85/310	2.0T	310 mm	225 mm	3.0 G/cm	100 mm DSV $\pm 5$ ppm	70 mm DSV 0.1 ppm	4.50 m	3.63 m

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July 29, 1988  
(received 8/6/88)

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

Dear Barry:

### Accuracy and Maximum Entropy

There have been many articles describing the improvement in appearance and in signal/noise ratio when free induction decays are processed by a maximum entropy method. There have also been descriptions of improvements in digital resolution without the artifacts of side-lobe generation produced by zero-filling. I had the need to get accurate peak positions in the second dimension of some 2D data sets and could not afford the time to collect sufficient sets of free induction decays. The data were treated by the Fougere modification of the Burg maximum entropy method and indeed much sharper lines were obtained with adequate digitization and no side lobes. To verify the accuracy of the peak positions I did the same data manipulation on synthetic FID's. As long as changes in frequencies for the lines of the synthetic FID were greater than the original digitization, peak positions in the final closely digitized spectrum agreed with the input values. When changes in frequencies of the input were smaller than the original digitization, there was no change in the peak position of the final spectrum even though the final lines were sharp enough to show such changes.

To summarize, in my hands at least although the maximum entropy method gives better looking spectra, the accuracy of peak positions is not improved.

Yours truly,

S. Brownstein  
Advanced Polymers  
and Composites

SB/jb

Canada

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*Professor of Chemistry: Robin K. Harris*

22nd July, 1988.  
(received 8/6/88)

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

Dear Barry,

## Quantitation of $^{29}\text{Si}$ MASNMR by Selective Saturation

Your "ultimatum" has had its usual (delayed) effect - hence this letter, which deals with a small part of our recent work on ceramic materials. A common problem for silicon nitride ceramic applications is high-temperature oxidation to give vitreous silica. The usual method of assessing the silica content of partially oxidised silicon nitride samples is to convert the vitreous silica into low-cristobalite by heat treatment, and then to estimate the relative proportions of  $\alpha\text{-Si}_3\text{N}_4$  and  $\text{SiO}_2$  by XRD. An alternative approach developed in this laboratory involves the selective saturation of  $^{29}\text{Si}$  NMR peaks. Spin-lattice relaxation times for  $^{29}\text{Si}$  in ceramics are typically minutes to hours, and, if quantitation is to be achieved simply, recycle delays of  $5 \times T_1$  for the longest component of the magnetisation must be used, requiring prior knowledge of  $T_1$ 's, and large amounts of spectrometer time. The  $T_1$  in vitreous silica is very much shorter than in  $\alpha\text{-Si}_3\text{N}_4$ , and the resonance is also much broader (Fig. 1a). Thus if the spectrum is acquired using a short recycle delay, the silica peak will be selectively enhanced (see Fig. 1b). This is highly advantageous because the width of the silica resonance is large relative to that for  $\alpha\text{-Si}_3\text{N}_4$ , and this makes it difficult to measure relative peak intensities exactly.

The peak intensity ratio,  $I_{\text{SiO}_2}/I_{\text{Si}_3\text{N}_4}$ , measured using the short recycle delay, can be compared with the ratio for a sample with known  $\text{SiO}_2$  content. In practice we achieve this by electronic mixing of the spectra of weighed samples of  $\alpha\text{-Si}_3\text{N}_4$  and vitreous  $\text{SiO}_2$  obtained under identical conditions. The method clearly depends upon the assumption that values of  $T_1$  for  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  are the same in reference and sample. Of course, this is not always so because of variable concentrations of paramagnetic impurities present in commercial  $\alpha\text{-Si}_3\text{N}_4$ . Thus, results must be treated with caution. Nevertheless, the method allows rapid estimation of degree of oxidation in samples containing more than ca. 10%  $\text{SiO}_2$ .

/cont.



- 2 -

We hope this snippet keeps us in good standing for another 9 months or so. Keep the Newsletters rolling to us!

Best wishes,

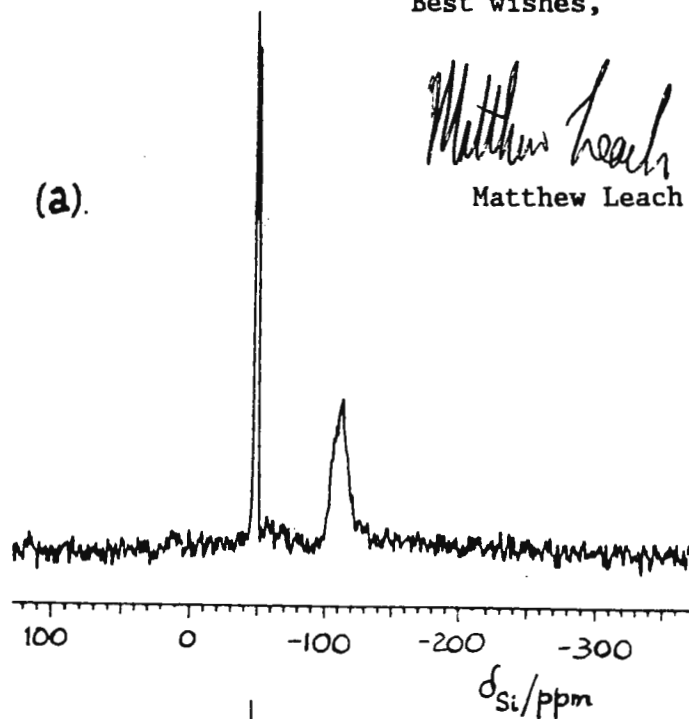
*Matthew Leach*

Matthew Leach

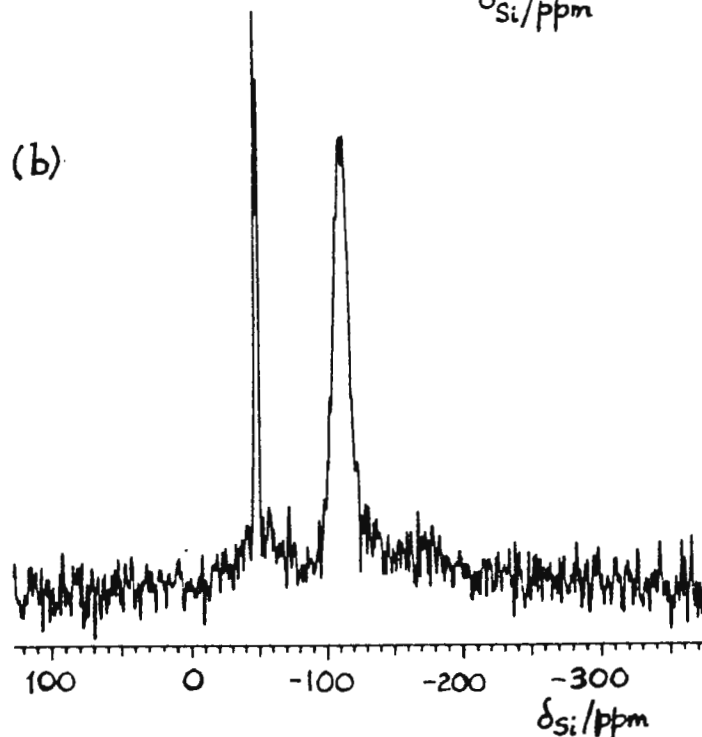
*Robin*

Robin Harris

(a).



(b)



$^{29}\text{Si}$  MASNMR spectra of a partially oxidised  $\alpha\text{-Si}_3\text{N}_4$  sample

(a) 120s recycle delay

(b) 10s recycle delay



UNIVERSITY OF VIRGINIA  
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Professor Bernard L. Shapiro  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94304

August 3, 1988  
(received 8/8/88)

HOHAHA and ROESY on GN Spectrometers without transmitter and decoupler phase coherence.

Dear Professor Shapiro:

When performing the HOHAHA (1,2) and ROESY (3,4) experiments one must use a spin locking field sometimes having a duration of ~100-300 ms. The General Electric GN-300  $^1\text{H}$  power amp is incapable of delivering pulses of this duration. While the low power observe transmitter will deliver pulses of the appropriate length, we found that the maximum field strength ( $\gamma B/2\pi$ ) was less than 1 KHz. This is too small to perform the experiments using a typical  $^1\text{H}$  bandwidth (~10 ppm). The  $^1\text{H}$  decoupler will deliver pulses of the appropriate magnitude and duration but unless the spectrometer has the high resolution  $^1\text{H}$  decoupler option, the pulses will not be coherent with the  $^1\text{H}$  observe channel and the experiments will fail.

The solution, which has been used by others including S. Lee of Proctor and Gamble and E. Zuiderweg et al. (5) is to connect the output of the low power observe amp (J9 on the low power switching module) to the input of the  $^1\text{H}$  decoupler power amp. The transmitter and decoupler cables at the front of the probe interface are removed and the decoupler cable is reconnected to the transmitter input. Thus the normal observe  $^1\text{H}$  amp has been replaced by the  $^1\text{H}$  decoupler amp. This allows one to generate the required nonselective pulses and spin-lock fields. In order to make sure that the  $^1\text{H}$  observe amp cannot be turned on we remove the cable at J7 of the low power switching module.

Before attempting the experiments one should set OC for low power operation. We find that a low power setting of 250 gives a 15 KHz field. Further increase in the low power setting did not substantially increase the field strength. Normally we use a field strength of 3 to 5 KHz and have not attempted any continuous spin locks at fields > 5 KHz. We have used a 15 KHz field at a 25% duty cycle for generating a pulsed (30° pulses) spin lock field as suggested by Kessler et al. (6). None of the spin locking conditions described above have resulted in amp or probe damage.

One may also use the  $^1\text{H}$  decoupler (minus final amp) to apply selective irradiation for solvent saturation or peak inversion. Selective inversion is required in the 1D versions of HOHAHA and ROESY. The  $^1\text{H}$  decoupler may be used by removing the cable at J1603 on the rear of the power amplifier chassis and connecting it directly to the decoupler input on the probe interface. We find with this configuration that a decoupler power setting of 63 gives a 12 Hz field. Thanks to Jerry Dallas of GE NMR for advice.

Sincerely,

Jeff Ellena

David Cafiso

Leslie S. Lepore

Sharon J. Archer

1. Bax, A. and Davis, D.G. (1985) J. Mag. Res. 65, 355.
2. Braunschweiler, L. and Ernst, R.R. (1983) J. Mag. Res. 53, 521.
3. Bax, A. and Davis, D.G. (1985) J. Mag. Res. 63, 207.
4. Bothner-By, A.A., et al. (1984) J. Am. Chem. Soc. 106, 811.
5. Zuiderweg, E.R.P., et al. (1986) J. Mag. Res. 70, 336.
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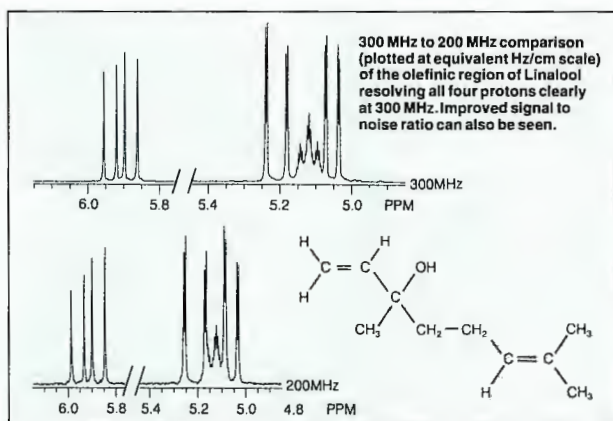
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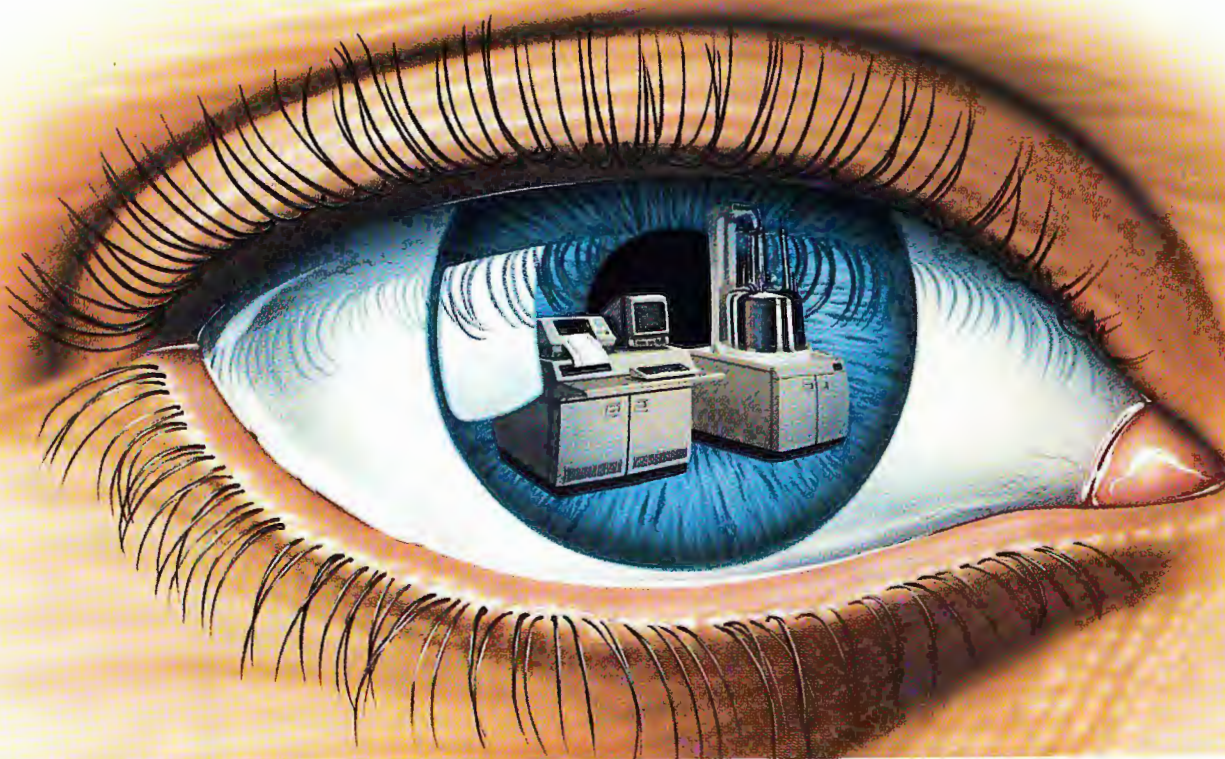
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Department of Chemistry

2145 Sheridan Road  
Evanston, Illinois 60208August 16, 1988  
(received 8/20/88)

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


Dear Barry:

We have been carrying out relaxation studies on the neurotransmitter acetylcholine chloride ( $\text{Me}_3\text{N}^+\text{CH}_2\text{CH}_2\text{O}(\text{CO})\text{CH}_3 \text{Cl}^-$ ). We have found that the mobility of the methyl groups is dependent on the basicity of the medium. Basic solvents such as water (in particular), dimethyl sulfoxide, and dimethylformamide reduce methyl mobility in both the trimethylammonium and (less so) acetyl groups, in comparison with mobility in the nonbasic solvent chloroform. Methyl mobility also is reduced slightly on the addition of a strong Lewis base such as tetrahydrofuran.

One possible explanation for these observations is that the methyl protons form weak hydrogen bonds ( $\text{C-H}\cdots\text{B}$ ) with basic sites on the solvents or additive molecules, since the methyl groups are attached to electron deficient centers. This nontraditional hydrogen bond has been suggested by Meot-Nur and Deakyne in this context. This conclusion has implications on how acetylcholine binds to its neuroreceptor.

Structural analogues of acetylcholine were examined in order to define the minimum structural requirements for this effect. These analogues included the ammonium ether  $\text{Me}_3\text{N}^+\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ , the ammonium ketone  $\text{Me}_3\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2(\text{CO})\text{CH}_3$ , the simple ammonium salt  $\text{Me}_3\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ , the ester  $\text{Me}_3\text{CCH}_2\text{CH}_2\text{O}(\text{CO})\text{CH}_3$ , and the hydrocarbon  $\text{Me}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ . Differences in aggregation in the various solvents are detected by the relaxation measurements, but this phenomenon does not influence methyl mobility.

Sincerely,

  
Joseph B. Lambert

Wojciech Schilf



Postal Address: Private Bag, Rotorua, New Zealand  
 Telegraphic Address: 'Frestra' Rotorua, N.Z.  
 Telex: NZ21080  
 Telephone: (073) 475-899 Fax: 479-380

14/5/4/11  
 RM:SD

4 August 1988  
 (received 8/11/88)

Dr Bernard L Shapiro  
 TAMU NMR Newsletter  
 966 Elsinore Court  
 Palo Alto  
 California 94303  
 UNITED STATES OF AMERICA

Dear Dr Shapiro,

**$^{119}\text{Sn}$  NMR OF TRIBUTYLTIN OXIDE PINUS RADIATA DEGRADATION PRODUCTS**

Recently we have become interested in the chemical breakdown of tributyltin oxide (TBTO) preservative in Pinus radiata timber. Previous chromatographic techniques have only determined the degree of butylation of these products. We set out to characterise these products by  $^{119}\text{Sn}$  NMR.

TBTO-treated timber was extracted with ether and concentrated to 5ml. The extract was investigated using an INVGATE sequence at 75 MHz on our AC-200. Figure 1 shows residual TBTO at 83 ppm and the predominant degradation products between 90 and 100 ppm.

As you may recall from our last contribution (355-82), Pinus radiata contains a great deal of free fatty acids and resin acids. It is proposed that the degradation products observed are tributyltin esters of resin and fatty acids, eg tributyltin acetate, abietate, oleate etc. This is further evidenced by  $^{13}\text{C}$  spectra of ether extracts of timber before and after TBTO treatment. There is an observable shift of 2-3 ppm to lower frequency by the carbonyl resonances of the fatty and resin acids in the tributyltin esters. This indicates increased shielding by the tin nucleus.

Other products at 145 ppm are as yet unidentified. One proposed product is tributyltin chloride, although there is not a large source of available chloride in Pinus radiata.

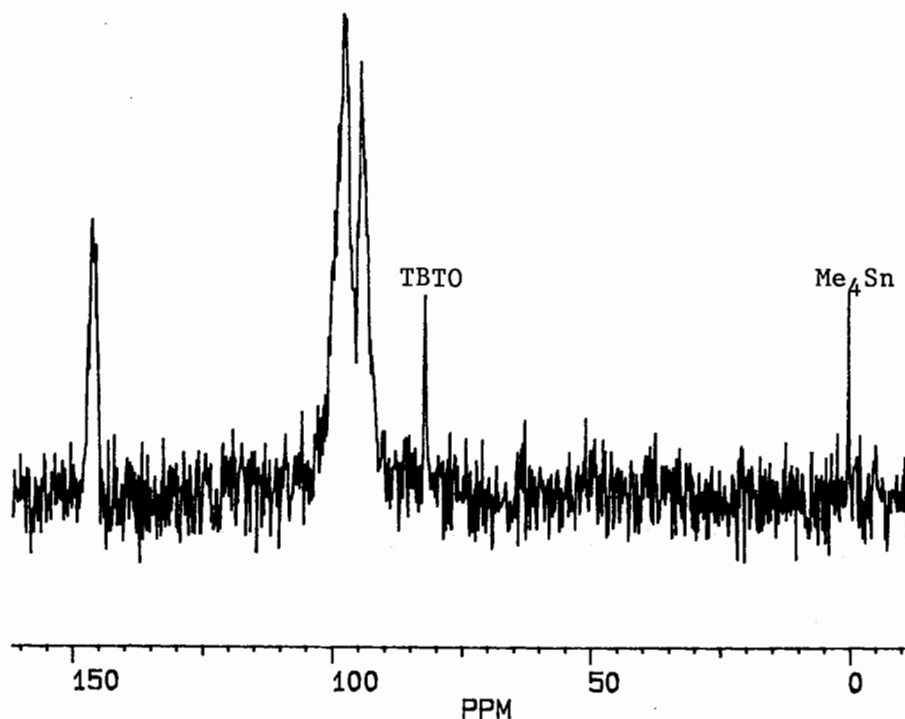
Despite this chemical breakdown you will be glad to know that there is no adverse effect on the preservative efficacy.

Yours sincerely,



Roger Meder  
for Director

FIG 1:  $^{119}\text{Sn}$  NMR spectrum of ether extract  
of TBTO-treated Pinus radiata





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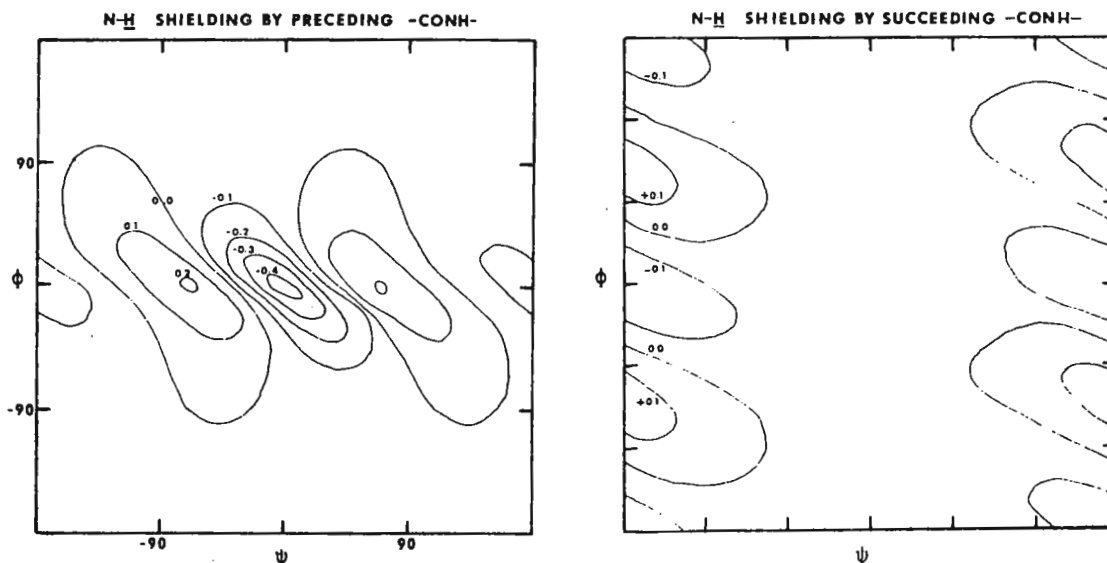
August 5, 1988  
(received 8/13/88)Dr. Bernard L. Shapiro, Editor  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303

Dear Barry:

The recent letter from D.M. Wilson (TAMU 356-48) regarding use of the magnetic anisotropy of formamide to estimate the conformation dependence of peptide  $\alpha$ -proton chemical shifts recalls that Dan Pilipauskas and I made the same attempt after the Tigelaar and Flygare paper appeared. Our plot of  $\alpha$ -proton isoshielding contours on the  $\phi - \psi$  plane is the same as Wilson's, with quantitative differences that probably arise from choice of bond parameters and dipole origin. We calculated a range of 0.32 ppm between extremes rather than 0.45, and would have estimated an upfield shift of ca. 0.1 ppm rather than 0.2 ppm on going from random to helix.

We never had any success in correlating predictions based on magnetic anisotropy with conformations for cyclic peptides. Conformation averaging apart, the principal reason for this failure is probably the much more important contribution from the electric field effect. (See C. Giessner-Prettre, M.T. Cung and M. Marraud, Eur. J. Biochem. (1987), 163, 79-87.)

We did the calculation for the peptide N-H protons as well, although the effects of magnetic anisotropy would be expected to be swamped by those of solvation and hydrogen bonding. Those plots, reproduced below, are obviously irrelevant to peptide conformation studies.

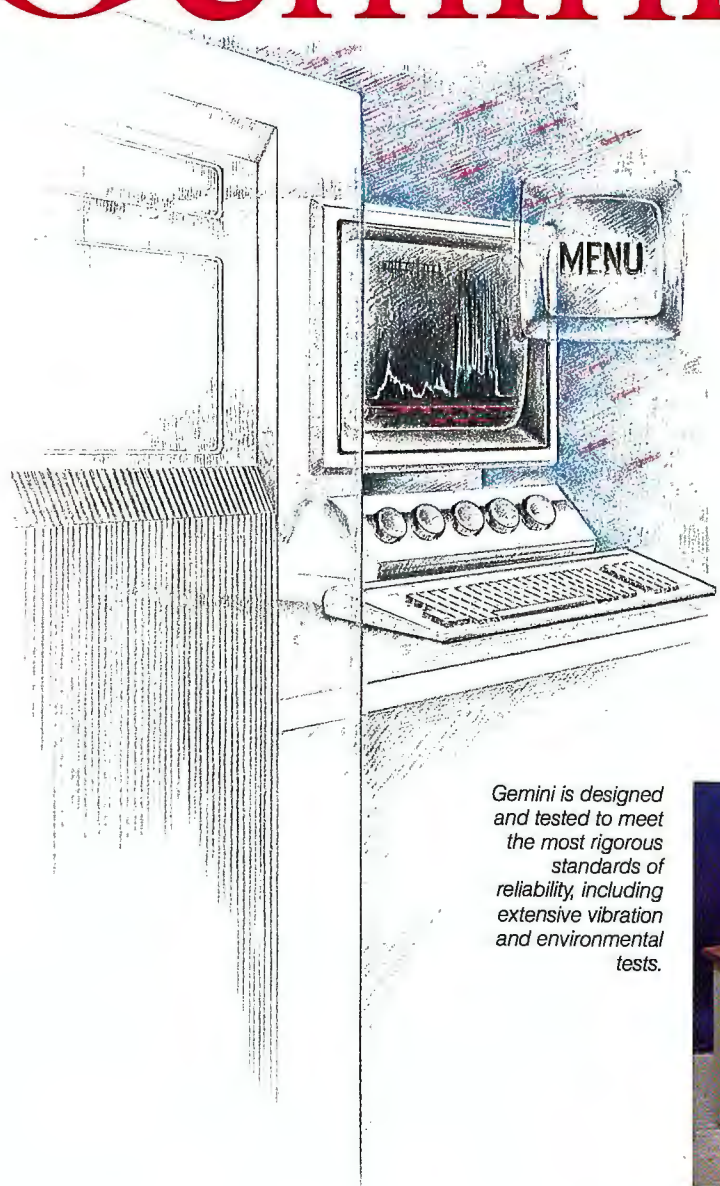


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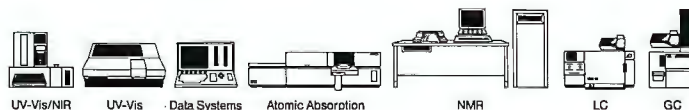
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July 22, 1988  
(received 8/1/88)

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

TITLE: Varian NMR file conversion to VAX

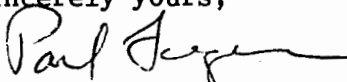
Dear Professor Shapiro,

Our laboratory processes NMR data off-line on a MicroVAX II with Dennis Hare's FTNMR program. To get both 1-D and 2-D datasets out of our Varian XL consoles, which use Motorola 68000 host CPUs, and onto the MicroVAX, we purchased the 9-track magnetic tape option from Varian. The FORTRAN program that I wrote for the VAX which reads the Varian tape and converts it to FTNMR format is too specialized to be of value in its entirety, but I would like to share some of the features I learned about Varian data formats to possibly spare others some grief and time.

The Varian TAPE command literally copies the sectors on disk associated with a file onto the tape in sequential order, except TAPE precedes the first disk sector image with a 512 byte header. The tape block size is  $20 \times 512 = 10240$  bytes, so the first block is 512 bytes of header followed by 19 disk sector images. We use the SVCF(filename) command on FID data, so that the following discussion applies only to conversion of files saved in this manner; SVF(filename) generates a different file structure that has not been analyzed. File information (experimental parameters) is contained in the first 12 sector images--followed by data representing FIDs. If the FID data is not complete in the last 7 sector images of the first tape block, another block is read. This block contains only FID data. As many blocks are read as necessary to access all the data in the file.

In translating the above described data patterns from Varian/Motorola conventions to VAX/FTNMR, I discovered the following: 1) The character data bit pattern in the tape header is the same as VAX FORTRAN--but in the file information sector images, Varian sets the eighth bit. Masking the eighth bit produces VAX compatible character data for file information. 2) The Varian data can be 16 or 32 bit integer (DP=N or DP=Y). The two bytes must be swapped for 16 bit Varian to convert directly to VAX FORTRAN 16 bit integer. For 32 bit integer conversion, swap byte 1 with byte 4 and byte 2 with byte 3. The FORTRAN "real" function converts either corrected integer type to 32 bit floating point as required by FTNMR. 3) Some file information is in Motorola 32 bit floating point format. Appended is a short function subprogram which performs this conversion. 4) Finally, one must know the precise location of information on the tape block and what it is meant to represent before any conversion is possible. The VAX/VMS "dump" command can be used for this purpose once a file is read from tape and stored as a VAX file. Some of the important parameter locations are: SW (floating point) is bytes 57:60 of disk sector 3; SF (floating point) is bytes 211:214 of disk sector 4; NP (floating point) is bytes 85:88 of disk sector 3; and DP (Varian character) is byte 295 of disk sector 3.

Sincerely yours,

  
Paul Fagerness

```

*      v float      Function to change 4 characters representing an XL
*      floating point (32 bit) number to VAX floating point (32 bit)
*
      REAL*4 FUNCTION v float(in)
      IMPLICIT      NONE
      CHARACTER*4    in, in_chars
      INTEGER*4      bits_32, exp_int, man_int
      INTEGER*4      exp_mask, man_mask
      REAL*4         frac
      PARAMETER      (exp_mask = '7F800000'X)
      PARAMETER      (man_mask = '007FFFFF'X)
      EQUIVALENCE    (in_chars, bits_32)

*      swap character bytes end for end
      in_chars(1:1) = in(4:4)
      in_chars(2:2) = in(3:3)
      in_chars(3:3) = in(2:2)
      in_chars(4:4) = in(1:1)

*      form the exponent and mantissa
      man_int = JIAND(bits_32, man_mask)
      frac = FLOATJ(man_int)/8388608 + 1      ! 2**23 = 8388608
      exp_int = JIAND(bits_32, exp_mask)
      exp_int = exp_int/8388608 - 127

*      and now form the number:
      v float = frac * 2**exp_int
      RETURN
      END

```

---

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Appointment to the Boswell Fellowship will be for one year and may be renewed by mutual agreement for an additional year. A third-year renewal may be possible in exceptional circumstances. The appointment will be administered by Caltech, and the appointee will be a member of the Caltech faculty. The research will primarily be carried on at HMRI, and possible areas of concentration will be *in vivo* NMR imaging and/or spectroscopy; for example, as applied to hepatic dysfunction, heart-muscle physiology, or the etiology and anatomy of brain lesions caused by strokes. Applicants are expected to have an M.D. or Ph.D. degree, or the equivalent. HMRI and Caltech are Affirmative Action-Equal Opportunity Employers, and encourage applicants from women and minority groups.

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Please apply to the Chairman of the Boswell Committee, Dr. Richard Bing, HMRI, 734 Fairmount Ave., Pasadena, CA 91105, and include a vita, publications list (if any), names of three references, and a statement of research interests in the NMR areas. We are very eager to obtain highly qualified applicants because we believe that this program has enormous potential, involving, as it does, the personnel and resources of both HMRI and Caltech.

John D. Roberts

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RESEARCH AND DEVELOPMENT

August 17, 1988 (received 8/22/88)

DJO-04-88

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

Dear Barry:

With the area of solid sample  $^{29}\text{Si}$  NMR spectroscopy continually expanding, it has become important to consider the issue of a proper reference, whether it be used internally or externally. In our laboratory, we have considered several compounds as references, and measured their chemical shifts against TMS by using a technique introduced by Earl and VanderHart (*J. Magn. Reson.* 1982, 48, 35-54). This technique involves inserting a capillary containing TMS down the center of a magic angle spinning (MAS) rotor and packing the unknown reference material around it. As Earl and VanderHart pointed out in their paper on  $^{13}\text{C}$  references, spinning concentric cylinders at the magic angle averages out the bulk susceptibility differences, to a first approximation. Using a direct polarization scheme, the spectrum thus acquired will display both the solid reference and the TMS in the capillary, as well as signals from the glass capillary. The chemical shifts for several compounds measured in this fashion are listed in Table 1. Two of these compounds (Q8Mg and DSS) have been used as references in the literature and the values given are listed in the Table. Recently, we obtained a sample of Tetrakis(trimethylsilyl)silane, TTMSS, from Strem Chemical (Newburyport, MA). This material gives a strong, sharp signal at  $-9.83 \text{ ppm} \pm 0.1 \text{ ppm}$  and a smaller signal at  $-135.36 \text{ ppm} \pm 0.1 \text{ ppm}$  (see attached spectrum). Its major advantages are its commercial availability and strong, sharp signal, while it suffers from the disadvantages of cost ( $\sim \$300/\text{g}$ ) and slow cross polarization ( $> 20 \text{ ms}$  to achieve full enhancement). We keep a rotor packed with TTMSS and use it as an external reference, which is sufficient for most applications.

Sincerely yours,

Dan O'Donnell

Steve Wharry

DJO:SMW:rk

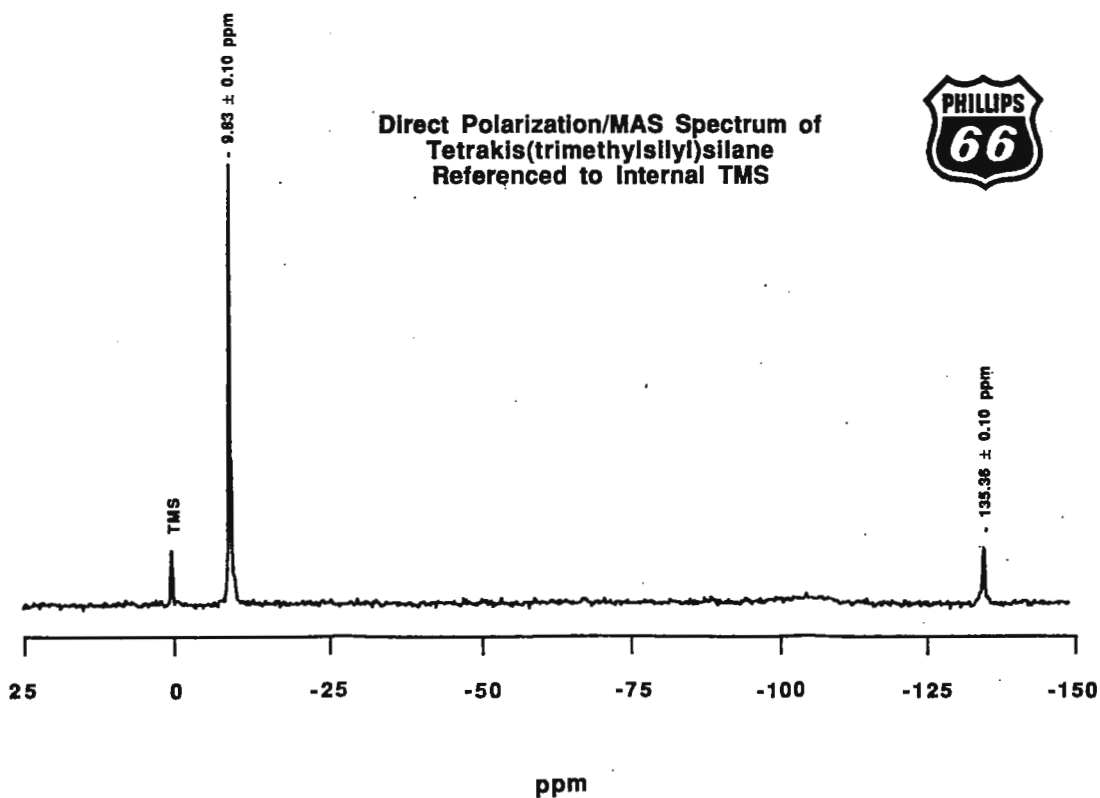


Table 1.  $^{29}\text{Si}$  Chemical Shifts of Some Reference Standards

<u>Compound</u>	<u>Shift(s) (ppm)</u>	<u>Lit. Value</u>	<u>Source</u>
Q8M8	11.85 $\pm$ 0.25 -108.23, -108.45 -109.20, -109.51	11.5a	W. Klemperer, U. Ill.
Tetrakis(trimethylsilyl)methane, TTMSM.	-1.39 $\pm$ 0.15		G. Maciel, Col. St. U.
Sodium 2,2-Dimethyl-2-silapentane-5-sulphonate, DSS	1.57 $\pm$ 0.25	-1.30b	MSD Isotopes
Quartz	- 107.20 $\pm$ 0.25	-107.4a	This laboratory
Tetrakis(trimethylsilyl)silane, TTMSS	- 9.83 $\pm$ 0.1 - 135.36 $\pm$ 0.1		Strem Chemicals

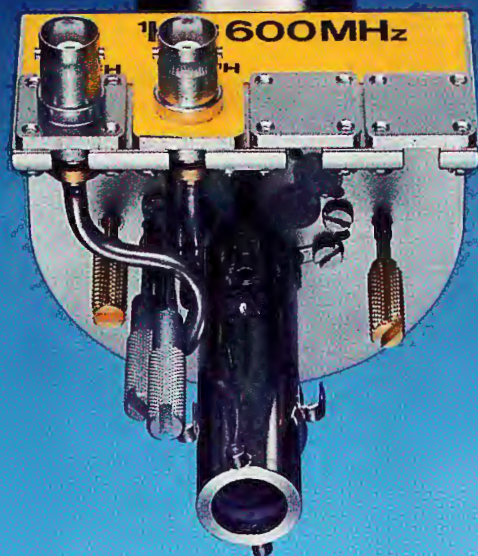
a. J. Am. Chem. Soc. 1980, 102, 4889.

b. J. Am. Chem. Soc. 1982, 104, 4859.





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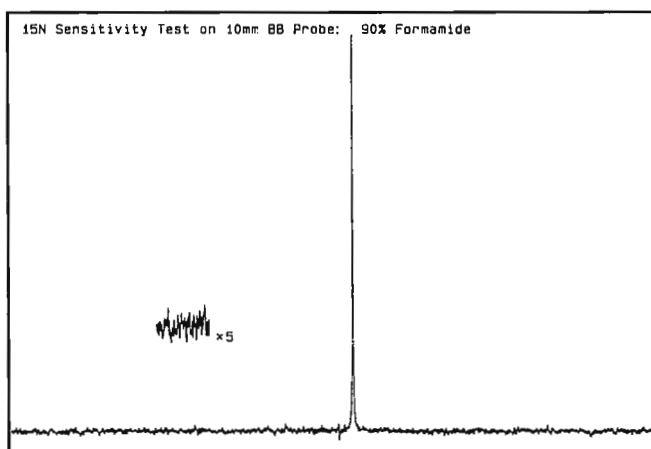
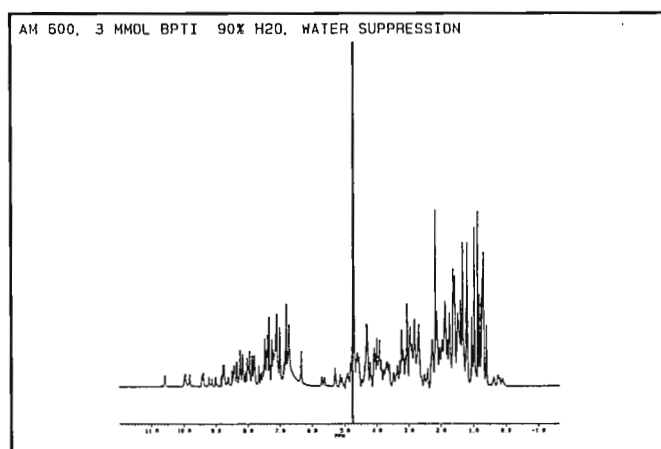
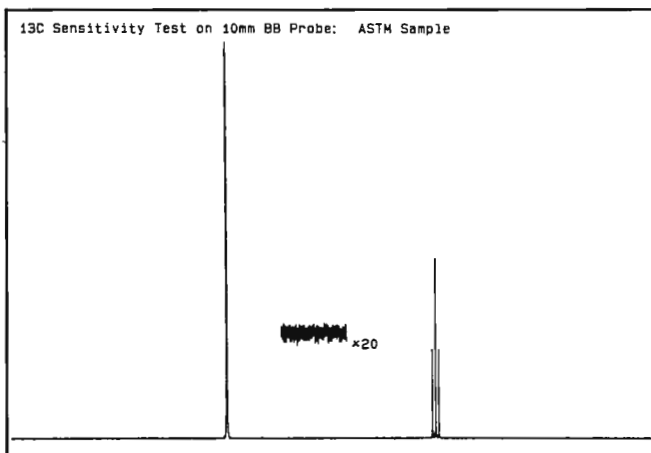
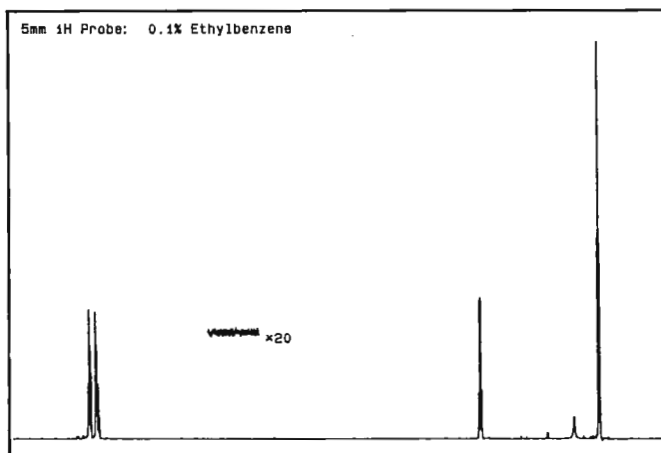
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		S/N	600:1	ASTM = 60% $\text{C}_6\text{D}_6$ in dioxane
Broadband (5mm)	$^{13}\text{C}$	S/N (ASTM)	220:1	FORM = Formamide ( $^1\text{H}$ decoupling without NOE)
		S/N (10% EB)	180:1	LINESHAPE: $^1\text{H}$ = $\text{CHCl}_3$ linewidth at height of $^{13}\text{C}$ satellite/at 20% this level
		lineshape	6/15	$^{13}\text{C}$ = $\text{C}_6\text{H}_6$ linewidth at 0.55%/0.11% of peak height
	$^{15}\text{N}$	S/N (FORM)	25:1	
Broadband (10mm)	$^{13}\text{C}$	S/N (ASTM)	650:1	
		S/N (10% EB)	375:1	
		lineshape	6/15	
	$^{15}\text{N}$	S/N (FORM)	80:1	
Resolution (all probes)			0.25 Hz	



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July 20, 1988

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

## BURNING HOLES IN YOUR SPECTRA

Dear Barry,

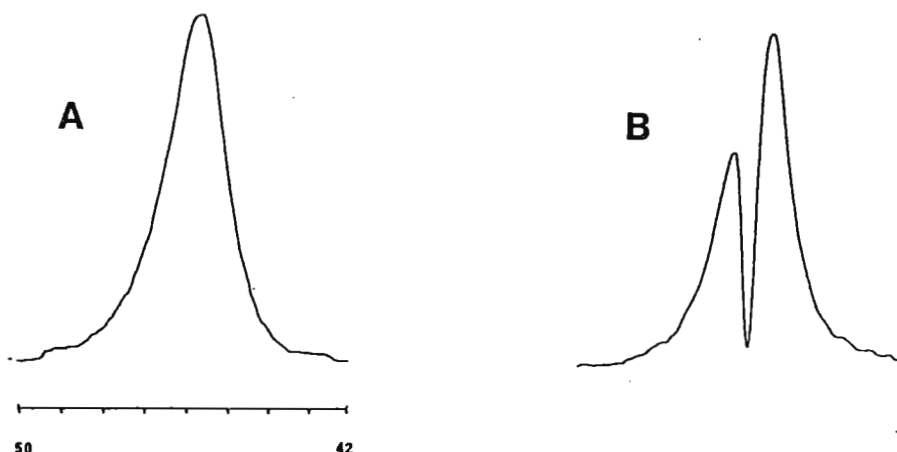
Lately we have been studying some polymer samples in which the McMaster Institute for Polymer Production Technology has been interested. In particular, we have been looking at poly(sodium acrylate) partially cross-linked with N,N methylene bisacryamide and swollen in water. As in most polymer spectra, the lines are broad, and we have found the amount of broadening useful in determining the amount of cross-linking (Polymer 29, 1338 (1988)). This raises the question of what causes the broadening — is it a decreased mobility giving shorter relaxation times and a homogeneously broad line; or is it a distribution of environments with relatively long relaxation times leading to inhomogeneous broadening?

To sort this out, we measured the linewidth at a series of magnetic fields starting from a WH90 magnet to an AM500. The linewidth increased linearly with field, giving a strong indication of inhomogeneous broadening, but to confirm this we also did a "hole burning" experiment on our WM250. The spectra below show the results on the methine line of the swollen gel: spectrum A being the normal one, and spectrum B having the hole burned into it with a DANTE sequence. This leaves no doubt that the broadening in this system is due to a distribution of chemical shifts.

A.D. Bain

D.R. Eaton

M. Mlekuz





Oklahoma State University

DEPARTMENT OF CHEMISTRY  
COLLEGE OF ARTS AND SCIENCES

STILLWATER, OKLAHOMA 74078-0447  
PHYSICAL SCIENCES 106  
405-624-5920

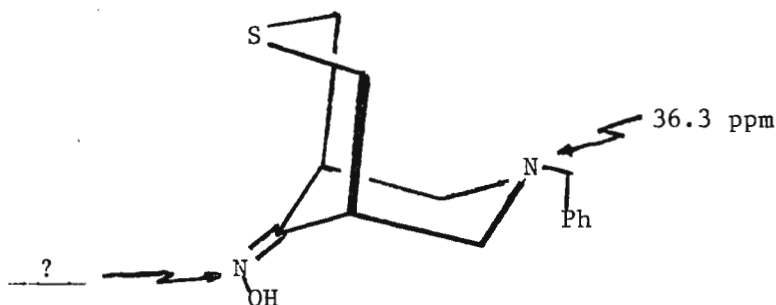
July 28, 1988  
(received 7/30/88)

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

TITLE:  $^{15}\text{N}$  NMR Data on Selected 3,7-Diheterabicyclo[3.3.1]-  
nonan-9-one oxime

Dear Barry:

Here is our contribution to the newsletter. We have been very busy installing a new NMR spectrometer and our other unit was used heavily for routine work. We have been investigating certain 3,7-diheterabicyclo[3.3.1]nonanes and derivatives and have noted some interesting  $^{15}\text{N}$  resonances or lack of such in some instances. 7-Benzyl-3-thiabicyclo[3.3.1]nonan-9-one was converted to its oxime by a modification of standard conditions. The solid product melted at 128.4-129.2°C and was supported by all spectral analyses and elemental analysis. However, the  $^{15}\text{N}$  NMR analysis revealed a signal at 36.3 ppm (external reference of  $^{15}\text{NH}_4\text{NO}_3$  and then to  $^{15}\text{NH}_3(\text{L})$ ) for the ring nitrogen but no signal was observed for the oxime nitrogen atom even after pulsing over a weekend. If anyone has any comments on this, we would welcome them. The  $^{15}\text{N}$  signals of oximes are not common or have we missed such data?



Sincerely yours,

K. Darrell Berlin  
Regents Professor



---

**Postdoctoral Position for NMR Spectroscopist*****Available Immediately***

Our lab is starting a project to analyze the conformation of biologically active peptides related to somatostatin, in collaboration with peptide chemists at a nearby Medical School. We plan to expand the use of new techniques in our analysis. We need a person who is familiar with the execution of 2D techniques, but not necessarily with peptides.

Please Contact: Andrew Waterhouse, Department of Chemistry, Tulane University, New Orleans, LA, 70118. Tel: 504-865-5573

---

---

**POSTDOCTORAL POSITION IN *IN VIVO* NMR**

The Pennsylvania State University College of Medicine, Department of Radiology has a position available immediately at the postdoctoral level for an individual with interest/experience in *in vivo* NMR spectroscopy/imaging in a number of projects in animals and man. Additional experience in biochemistry, physiology, or RF electronics is highly desirable. Current instrumentation includes a Bruker AM-400 WB spectrometer with microimaging and a 1.9 T, 26 cm horizontal bore spectrometer. Acquisition of an additional research dedicated whole body spectrometer is planned for 1989. Applicants should submit letter of application, curriculum vitae, and the names of three references to: Dr. Michael B. Smith, Department of Radiology, P.O. Box 850, Hershey, PA 17033. An Affirmative Action/Equal Opportunity Employer. Women and Minorities are encouraged to apply.

---

**Syracuse University has a STAR Technologies ST-100 100 MFLOP array processor for sale.**

The 32-bit ST-100 is a high-performance array processor. It attaches to general-purpose computers for signal processing, image processing, simulation, geophysical applications, and general scientific computing. The ST-100 offered for sale is fully functional and eligible for hardware maintenance. It is equipped with 1.5 Megawords of 32 bit memory, an interface for a VAX Unibus and software for DEC VAX computer hosts, other interfaces are available from STAR. The ST-100 array processor software provides two levels of optimization. The Array Processor Control Language (APCL), a subset of ANSI FORTRAN 77 with language extensions, makes the ST-100 Array Processor easy to use and includes a large Application Support Library. Additionally, there is further optimization available from the Macro Assembly Language. The list price for this current-model system is over \$300,000. The ST-100 will be sold for the best offer received before November 1, 1988 (min. \$95,000). For further information contact either Prof. George C. Levy or Dr. Bill Curtiss, (315) 443-1021, Chemistry Department, Syracuse University, Syracuse, NY 13244-1200.



**--ANNOUNCEMENT--****--AND CALL FOR CONTRIBUTED POSTERS--****THE SECOND MISSOURI MAGNETIC RESONANCE SYMPOSIUM (MMRS-II)**

HOST: DAVID W. LARSEN

TUESDAY, OCTOBER 25, 1988

UNIVERSITY OF MISSOURI-ST. LOUIS (UMSL)  
 8001 NATURAL BRIDGE ROAD  
 ST. LOUIS, MISSOURI 53121

The planned one day program includes five invited lectures plus a poster session (contributed). Refreshment breaks will be provided, lunch and housing are available at a small cost.

The tentative list of speakers includes:

Brian Reid, University of Washington  
 William Hutton, Monsanto Co.  
 Joseph Ackerman, Washington University  
 Tuck Wong, University of Missouri-Columbia  
 Art Lind, McDonnell Douglas

*AT THIS TIME WE ARE CALLING FOR POSTERS FOR ALL AREAS OF MAGNETIC RESONANCE.*

COST: \$5.00 per person, students free, luncheon served at a small cost.

If you need further information, contact Dave or me at the address below.

David W. Larsen  
 Department of Chemistry  
 University of Missouri, St. Louis  
 8001 Natural Bridge Road  
 St. Louis, Mo. 63121  
 314-553-5341

Frank D. Blum  
 Department of Chemistry  
 University of Missouri, Rolla  
 Rolla, Mo. 65401

314-341-4451 Bitnet:C2828@UMRVMB

---

Please return to: Frank D. Blum

\_\_\_\_\_ I (we) plan to attend the **SECOND MISSOURI MAGNETIC RESONANCE SYMPOSIUM**.

\_\_\_\_\_ I (we) plan to present a poster entitled: \_\_\_\_\_

\_\_\_\_\_ Please send us further information.

Also send information to the following person(s):

NAME: \_\_\_\_\_  
 ADDRESS: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

NAME: \_\_\_\_\_  
 ADDRESS: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_



## Probe Repair Service

**Do you need faster service?** If so, FMR should be your first choice for repair or adjustment of an existing probe. FMR is prepared to service probes from all vendors. Our engineers and technicians can provide you a probe repair service with:

**Quality** To us, quality work means understanding and solving your probe problem the first time you ship it to us. This requires good communication, and at FMR you will be able to speak directly to the engineer doing the work. We won't ship it until it's fixed right.

**Experience** Since we service all vendor's probes, we have a broader perspective on probe problems. Every person who handles your probe has designed, built, and tested probes themselves.

**Speed** We know you need your probe back promptly. We're prepared to set and meet turn-around times to get you back on the air quickly.

**Cost** Our rates are very competitive.

So the next time you need work done on a probe, think of Fremont Magnetic Resonance. We can provide the best means to perform of the probe maintenance below:

Replace capacitor  
Replace broken insert  
Fix or modify capacitor stick  
Replace broken or "soft" dewer  
Minor "surgery" on a probe

## High Resolution Probes

FMR offers a wide variety of new high resolution probes for most NMR systems and upgrades for existing probes to a higher performance level or to do different nuclei. This is usually done for much less than the cost of a new probe. This option is available for most NMR probes including the top loading NT Series probes. Performance specifications based on a console in good working order with a noise figure of less than 2 dB are shown in the summary below. Call for more information or different requirements.

### 5mm 1H Probe

90° Pulse 10 us @ 50 Watts	Sensitivity (0.1% EB)
Resolution 0.2 Hz (ODCB)	200 MHz 80:1
Lineshape 10/20 (CDCI3)	300 MHz 160:1
	360 MHz 220:1
	400 MHz 300:1
	500 MHz 400:1

### Reverse Polarization Transfer Probe

$^1\text{H} \{^{31}\text{P}-^{15}\text{N}\}$ 5mm Probe	5mm	10mm
90° Pulse @ 50 Watts	15us	25us
Resolution (ODCB)	0.25	0.4
Lineshape (CDCI3)	10/25	18/40
Gamma $\text{H}_2$ (10W)		
$^{15}\text{N}$	2KHz	1KHz
$^{13}\text{C}$	3KHz	2KHz
Sensitivity (0.1%EB)		
	200 MHz 60	100
	300 MHz 120	200
	360 MHz 170	280
	400 MHz 200	330
	500 MHz 300	500

### Broadband Probes

High Band broadband probes cover the range from  $^{31}\text{P}$  to  $^{15}\text{N}$  for solutions up to 0.2 M salt.  $^{31}\text{P}$  performance is 15% less for narrow bore magnets.

5mm	200	300	360	400	500
$^{31}\text{P}$	30	60	85	100	150
$^{13}\text{C}$	30	60	85	100	150
$^2\text{H}$ NA = 4	5	10	14	16	25
$^{17}\text{O}$ NA = 100	20	40	55	65	80
$^{15}\text{N}$	4	8	10	12	16

### 10mm

$^{31}\text{P}$	130	260	340	375	450
$^{13}\text{C}$	150	300	360	400	500
$^2\text{H}$ NA = 4	15	30	40	50	60
$^{17}\text{O}$ NA = 100	110	220	270	300	400
$^{15}\text{N}$	15	30	35	40	50

### 12mm

$^{31}\text{P}$	150	300	400	500	550
$^{13}\text{C}$	180	360	500	600	700
$^2\text{H}$ NA = 4	20	40	50	60	75
$^{17}\text{O}$ NA = 100	125	250	300	350	500
$^{15}\text{N}$	15	30	40	50	60

### 20mm

$^{31}\text{P}$	250	500	600	750
$^{13}\text{C}$	300	600	700	800
$^2\text{H}$ NA = 4	30	60	70	90
$^{17}\text{O}$ NA = 100	180	350	450	550
$^{15}\text{N}$	25	50	70	80

## Fun with your old shims

Even if you haven't upgraded your high-resolution system to microscopic imaging, you can still do some useful imaging with your standard shim coils. But instead of imaging some dreary old samples, you will be imaging a reference to analyze (and maybe improve) your probe shimming. In this note we will show how to determine if your probe is correctly positioned. In later articles we'll explain how to analyze your  $H_0$  field shape.

Here's how it works. A regular imaging experiment assumes a homogeneous field to translate image intensity to sample proton density variations. Our shimming experiment will use a uniform density sample to translate the variation in line intensity into field inhomogeneity. If you apply a static  $z$  gradient to a uniform sample, the resultant spectrum will be a rectangle convolved by the natural lineshape if both the  $H_1$  and  $H_0$  homogeneity are good. For a gradient larger than the natural linewidth, the resultant spectra should look like the solid line of figure 1 for both positive and negative gradients. We call these  $Z_1$  gradient spectra. (The properly shimmed spectrum is shown as a dotted line.)

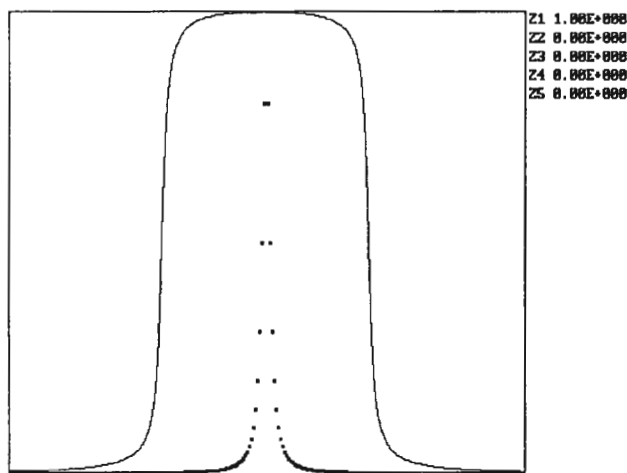


Figure 1.

Reference Lorentzian (dotted) and  $Z_1$  gradient spectrum simulation.

You can produce a  $Z_1$  gradient spectrum on your instrument by the following procedure: 1) Start with a well shimmed probe and a compound with a single resonance line less than 2 Hz wide (for proton probes we often use  $\text{CHCl}_3$ ). 2) Turn the lock to standby, record a spectrum, and set the offset to zero for the (single!) peak. 3) Decrease the  $Z_1$  shim setting by an amount sufficient to produce a 200 Hz wide line (by trial and error). 4) Record that spectrum. 5) Record a spectrum with the  $Z_1$  shim increased by the same amount over the reference value.

The positive and negative gradient spectra that you produce should have the same first moment (center of 'mass'), if the observe coil is centered in the gradients. They should also be symmetric about their center. If you know the sample's active length (either because you used a vortex plug, or from knowledge of the coil length) you can calculate the gradient strength in Hz/mm, and from this calculate any offset of the coil from the shim center. Suppose the active length of the sample (constrained by vortex plugs) is 10mm. Therefore this particular setting of the shim DAC corresponds to 20 Hz/mm. If the first moments of the two spectra differ by, say, 50 Hz, the coil is misplaced by 2.5 mm.

But is it too high or too low? One easy way to tell is to pull the sample up so that it is half way out of the coil while the  $Z$  gradient is still on. If the first moment increases, the coil is too high; if it decreases it is too low.

Real probes seldom look as nice as figure 1. An example from a good  $^1\text{H}$  probe is shown in figures 2a and 2b. Notice

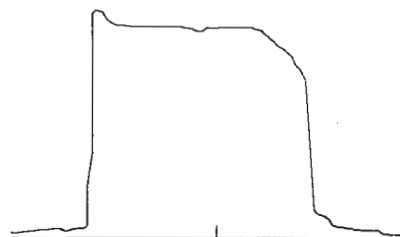


Figure 2a.  $+Z_1$  gradient,  $^1\text{H}$  probe

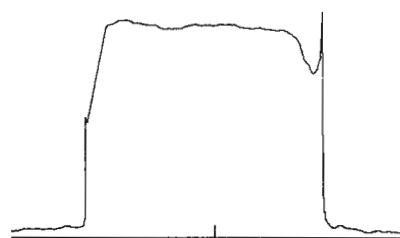


Figure 2b.  $-Z_1$  gradient,  $^1\text{H}$  probe

the spike in spectrum 2b. In contrast to this result, in most cases you will see precisely two spikes (in total) among these two spectra; in the next discussion on this topic we'll discuss how this effect and others come about.



Unocal Science & Technology Division  
 Unocal Corporation  
 376 South Valencia Avenue, P.O. Box 76  
 Brea, California 92621  
 Telephone (714) 528-7201



May 26, 1988 AR 88-87  
 (received 8/25/88 [sic])  
 Professor Bernard L. Shapiro  
 Department of Chemistry  
 Texas A&M University  
 College Station, Texas 77843-3255

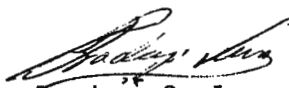
Dear Professor Shapiro:

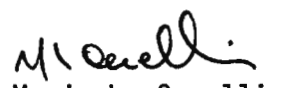
Comments On  $^{29}\text{Si}$  MAS NMR Analysis of Offretite-Erionite  
 Family of Zeolites

It is well known that  $^{29}\text{Si}$  spectra of zeolites obtained under simple MAS (magic angle spinning) conditions can typically consist of up to five resonances separated by  $\sim 5$  ppm. This difference in isotropic chemical shifts is caused by the presence (or absence) of aluminum in the first coordination sphere of a  $\text{SiO}_4$  tetrahedral unit. There is evidence in the literature, however, that presence of inequivalent crystallographic sites also contribute to chemical shift dispersion. Offretite and Erionite are two end members of a zeolite family that represent a unique class where the magnitude of deshielding caused by either, is approximately the same. We have recently studied a series of these zeolites (synthesized with different organic templates) using a IBM AF-270 spectrometer equipped with a solids probe from Doty Scientific.

Experimental  $^{29}\text{Si}$  signals were resolved into a superposition of Gaussian components using the LINESIM program (courtesy of Dr. Peter Barron, Griffith University, Brisbane, Australia) on the Aspect 3000 computer (see Figure). The assignments of the signals has been a matter of conjecture in the past. Based on the recent results reported by Fyfe and co-workers (Zeolites, 1985, 219), the Si/Al ratios were computed assuming random distribution of aluminum over two inequivalent crystallographic sites present in a ratio of 2:1. Our results show that this assumption may not be justified in all cases (see Table). The discrepancy between the computed ratios and chemical analyses suggests non-random aluminum distribution. Thus, in order to study details of dealumination processes in such systems, a more accurate model is needed that considers both specific and random siting of aluminum.

Yours sincerely,

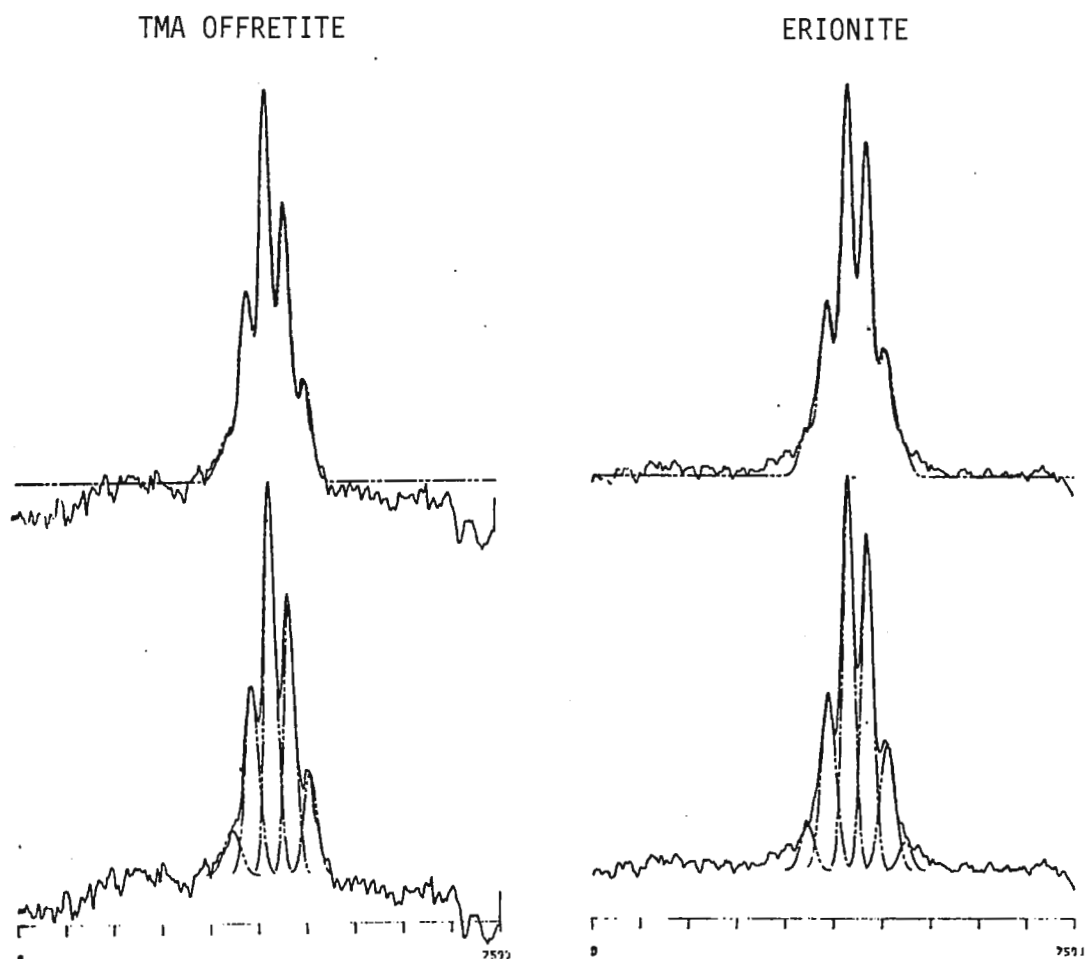
  
 Pradeep S. Iyer  
 Research Chemist

  
 Mario L. Occelli  
 Research Associate

PSI/MLO:lvb  
 attach.

P.S. Please credit this contribution to Dr. P. S. Iyer.

FIGURE



TABLE

*****		
Sample	Si/Al ratios	
	NMR	Chem
*****		
Na,K, TMA (tetramethyammonium)	3.1	3.9
Na,K, CC (choline chloride)	3.7	4.1
Na,K, BTEA (benzyltriethyl ammonium)	5.8	5.8
Na,K, DABCO (1,4-diazabicyclo(2.2.2)octane	3.3	4.8
ZSM-34	3.7	5.9
ERIONITE (natural sample from Rome, Oregon)	3.1	3.7

\*\*\*\*\*

## HIGH PERFORMANCE MR IMAGING SOFTWARE



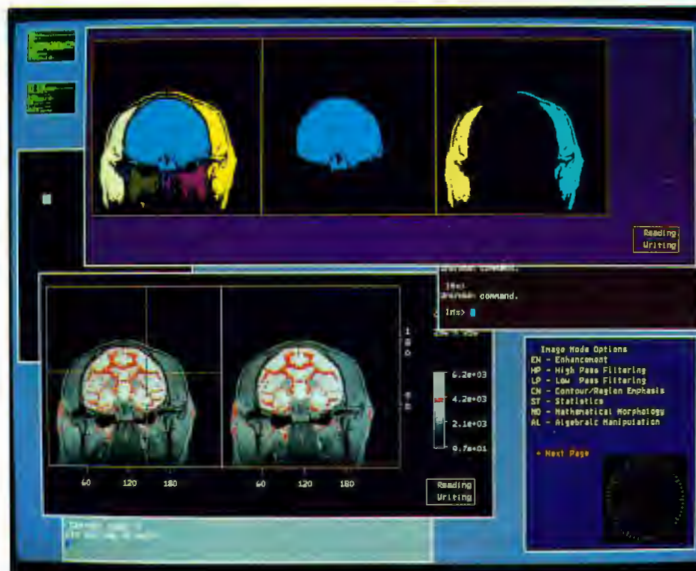


# NMR2/IMAGE

## Advanced enhancement

### 1

## Versatile Image Display



The versatility of NMRI's SpecStation™ environment provides flexible screen configurations to optimize display of intermediate processing results. Mouse-driven real-time inspection tools are supported to allow gray level manipulations which increase contrast and outline features of interest. The lower set of images at the left illustrates the effect of selective intensity range display, which highlights structures of uniform brightness. An example of gamma-curve remapping, which increases overall brightness, is applied to the rat torso image shown below.



### 2

## Enhancing Structural Definition



IMAGE includes a variety of contrast enhancement techniques to allow better perception of fine details and subtle changes in brightness. Options include:

- Contour Extraction
- Region Emphasis
- S/N Ratio Improvement
- Adaptive Filtering
- Gray Level Morphology
- User-Defined Convolution Kernels
- Fast 2D Fourier Processing
- Histogram Equalization

The upper pair of images illustrates the source and result of contrast enhancement via histogram equalization. The lower pair shows a source image with its corresponding power spectrum; the vertical artifact in the original image is revealed as a horizontal structure in the power spectrum. Frequency processing of the power spectrum can effectively remove the artifact in the original image.



# Advanced techniques for editing and measuring MR images.

3

## Counting and Measuring Binary Patterns



An automated segmentation procedure based on the analysis of the intensities in a monkey brain image has produced the binary patterns shown here. A labeling procedure can be used to identify each connected component. A binary editing capability allows the user to point to the labeled structures and extract characteristic region parameters such as:

- Area, Perimeter
- Circular Shape Factor
- Length, Width
- Center of Gravity
- Fractal Dimension

4

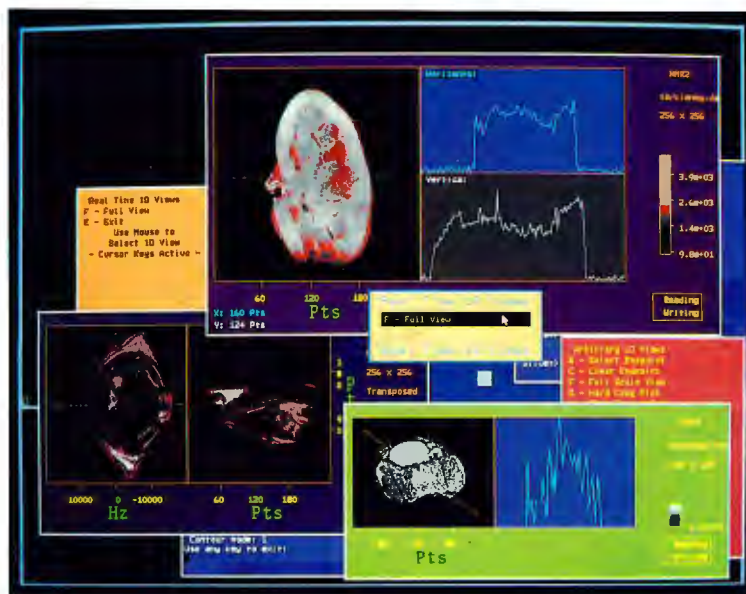
## Advanced Restoration Methods



Several deconvolution techniques, based on the maximum entropy and other criteria are provided. Here, the original, leftmost images are enhanced through Gaussian deconvolution, to yield results with improved structural definition drawn in the right half of the display. Other enhancement techniques are available, including Principal Component Analysis for both noise reduction and composite filtering of images and 2D NMR spectra.

## 5

## Gray Value Measurement



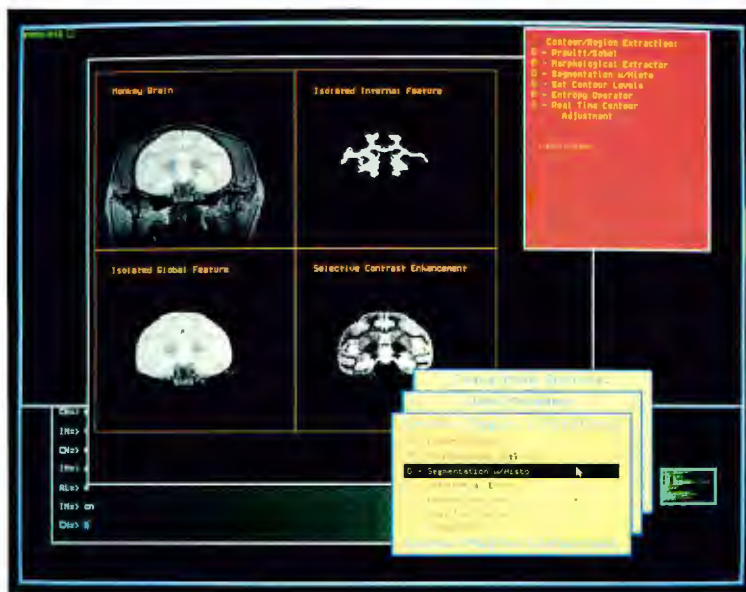
Real-time inspection and analysis of image intensities includes extraction and display of horizontal, vertical and arbitrarily oriented slices. Slices are selected graphically via mouse driven crosshairs. In addition, mouse-activated pop-up menus allow for fast and efficient use of these real-time tools as well as easy operation of all IMAGE facilities.

IMAGE measurement tools provide:

- Mean, Variance Measurement
- Histogram Analysis by Shape Modeling
- S/N Ratio Estimation
- Contrast Measurement
- Pixel Intensity Reporting
- Cross-sectional 1D Display
- Correlation Measurement

## 6

## Region of Interest Selection and Processing



Powerful adaptive algorithms utilize regional processing to take advantage of local stationarity of image features. In this manner, filters can be automatically adjusted to yield optimal results for the areas of interest. In this example, the central surface of a monkey brain image has been selected and isolated for local contrast enhancement. Free form contour tracing via the mouse is also supported for interactive definition of regions of interest.

**The LAB ONE™ NMR2/IMAGE program is an advanced, high performance research system that runs on UNIX/VMS workstations.**

For further information contact:

**nMRI:**

**New Methods Research, Inc.**

719 East Genesee Street  
Syracuse, New York 13210  
(315) 424-0329 FAX: (315) 424-0356



(619)-457-9720 ... office

Mark Rance, Ph.D.

Assistant Member

Department of Molecular Biology

Research Institute of Scripps Clinic

10666 North Torrey Pines Road

La Jolla, California 92037

August 11, 1988  
(received 8/17/88)

Dr. Bernard L. Shapiro, Editor/Publisher

TAMU NMR Newsletter

966 Elsinore Court

Palo Alto, CA 94303

### Resonance Inversion in TOCSY Experiments

Dear Dr. Shapiro:

The TOCSY experiment [1,2] (also referred to by some as HOHAHA) has become a very useful tool for resonance assignment in high-resolution proton NMR spectroscopy of macromolecules. In performing a TOCSY experiment, one of the most obvious parameters which must be chosen is the length of the mixing time. The specific choice made will determine the extent of coherence transfer through the spin systems under study. Unfortunately, it becomes exceedingly tedious to derive an analytical solution for the evolution of coherences in a TOCSY experiment for spin systems more complicated than  $AB_2$ . However, a computer simulation of this experiment is straightforward, especially if the mixing Hamiltonian consists only of the isotropic scalar coupling terms; experimentally one would apply some multi-pulse sequence such as MLEV-16 effectively to create such a Hamiltonian. In the simulation program we have written, the eigenvalues and eigenfunctions of the mixing Hamiltonian are calculated, and the matrix representation of the initial density operator and desired magnetization components are determined in the eigenbase of the mixing Hamiltonian. The time-dependence of the density matrix is easily calculated from knowledge of the eigenvalues of the Hamiltonian, and the evolution of the desired components is then simply the trace of the product of the density matrix and the specified component, such as the in-phase magnetization  $I_{i\alpha}$  ( $i$ =desired spin,  $\alpha$ =x,y or z). Systems of at least ten spins can easily be simulated with such a program, due to simplifications arising from the fact that the coherence order of a system is conserved in the isotropic mixing process. We have employed this program to simulate the evolution of coherences in TOCSY experiments for a variety of spin systems. One of the most interesting observations we have made is the fact that negative peaks can be obtained in spectra for systems of at least five spins. It has generally been assumed that all in-phase components (i.e. arising from  $I_{i\alpha}$  terms) in a TOCSY spectrum always have the same algebraic sign as the initial magnetization at the beginning of the mixing period. However, our simulation results have shown that this is not true in general. In the accompanying figure we show a simulated 2D TOCSY spectrum (using a program called SPINNER, written previously in this laboratory) for a five spin system ABCDE, with  $J_{AB}=J_{BD}=J_{CE}=12$  Hz,  $J_{AC}=J_{BE}=J_{CD}=4$  Hz,  $J_{BC}=J_{DE}=-15$  Hz and  $J_{AD}=J_{AE}=0$ . The mixing time used was 157.5 ms; this value was chosen with the aid of the simulation program described above. Both positive and negative contour levels have been plotted. The circles indicate peaks which are negative; this is illustrated more clearly by the slice taken through the contour plot, parallel to the  $\omega_2$  axis at the  $\omega_1$  shift of spin E. The presence of negative peaks is probably not a serious problem in most TOCSY experiments, since they tend to appear at relatively long mixing times. However, such peaks do have important consequences for the process of trying to identify artefactual peaks in rotating-frame NOE spectra.

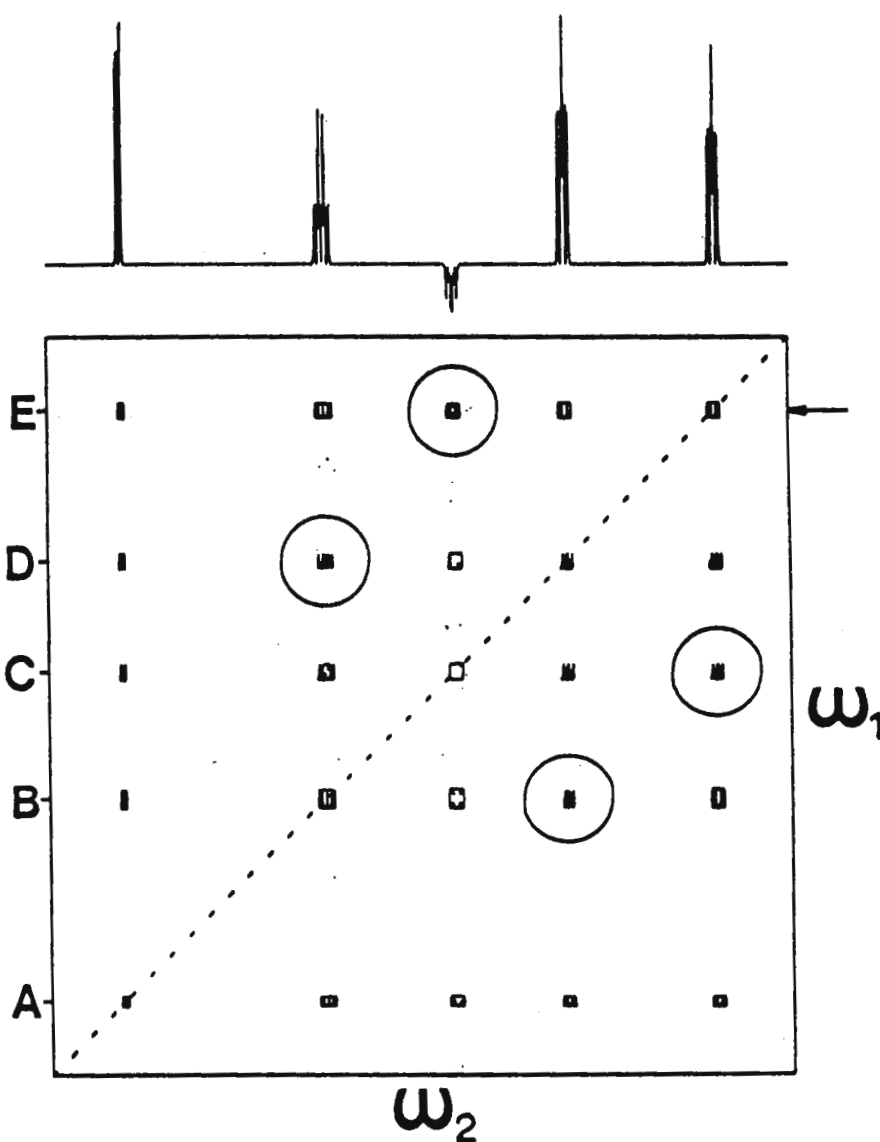
Please credit this contribution to the account of Dr. P.E. Wright.

Sincerely,

*Mark Rance*

Mark Rance

- [1] L. Braunschweiler and R.R. Ernst, J. Magn. Reson. 53, 521 (1983).
- [2] A. Bax and D.G. Davis, J. Magn. Reson. 65, 355 (1985).



# Stable Isotope Labelled Biomass Products

from



in collaboration with



*Isotec Inc.*, in collaboration with **Martek Corp.**, can now offer algal-produced biomass and derived products labelled with carbon-13 and deuterium; other stable isotope labelled compounds and mixtures will also be available. **Please let us know what you need and want –**  
– compound(s) or mixture(s), label(s), quantity(ies), etc.

CAT. NO.	PRODUCT	QUANT.	PRICE U.S. \$*
83-30003	D-Glucose- <sup>13</sup> C <sub>6</sub> 99 atom % <sup>13</sup> C	1g 10g 25g	525. 5000. 11875.†
83-30013	D-Glucose- <sup>13</sup> C <sub>6</sub> 30 atom % <sup>13</sup> C	1g 10g 25g	325. 3000. 7125.†
82-30011	D-Glucose-C-d <sub>7</sub> (98 atom % D)	†	†
83-61007	High-protein algal biomass 90+ atom % <sup>13</sup> C ca. 70% crude protein	1g 10g 25g 50g	250. 2000. 4750. 8750.†
82-61001	High-protein algal biomass 98 atom % D ca. 70% crude protein	†	†

## Typical approximate amino acid analysis (%)

Ala 6	Cys 1	His 1	Lys 4	Pro 3	Trp 1
Arg 6	Glu 9	Ile 4	Met 2	Ser 4	Tyr 5
Asp 6	Gly 3	Leu 6	Phe 4	Thr 4	Val 6

83-42023	Hexadecanoic Acid- <sup>13</sup> C <sub>16</sub> (Palmitic Acid) (99 atom % <sup>13</sup> C)†	†
83-42024	Hexadecanoic Acid- <sup>13</sup> C <sub>16</sub> (Palmitic Acid) (30 atom % <sup>13</sup> C)†	†
83-42025	Octadecanoic Acid- <sup>13</sup> C <sub>18</sub> (Stearic Acid) (99 atom % <sup>13</sup> C)†	†
83-42026	Octadecanoic Acid- <sup>13</sup> C <sub>18</sub> (Stearic Acid) (30 atom % <sup>13</sup> C)†	†
83-42021	Oleic Acid- <sup>13</sup> C <sub>18</sub> (99 atom % <sup>13</sup> C)	†
83-42022	Oleic Acid- <sup>13</sup> C <sub>18</sub> (30 atom % <sup>13</sup> C)	†

*Isotec Inc.* also has stock of a variety of specifically <sup>13</sup>C-labelled amino acids as well as

83-30000	D-Glucose-1- <sup>13</sup> C	1g	325.
	99 atom % <sup>13</sup> C	5g	900.
		10g	1400.
		25g	3250.†

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# $^{17}\text{O}$

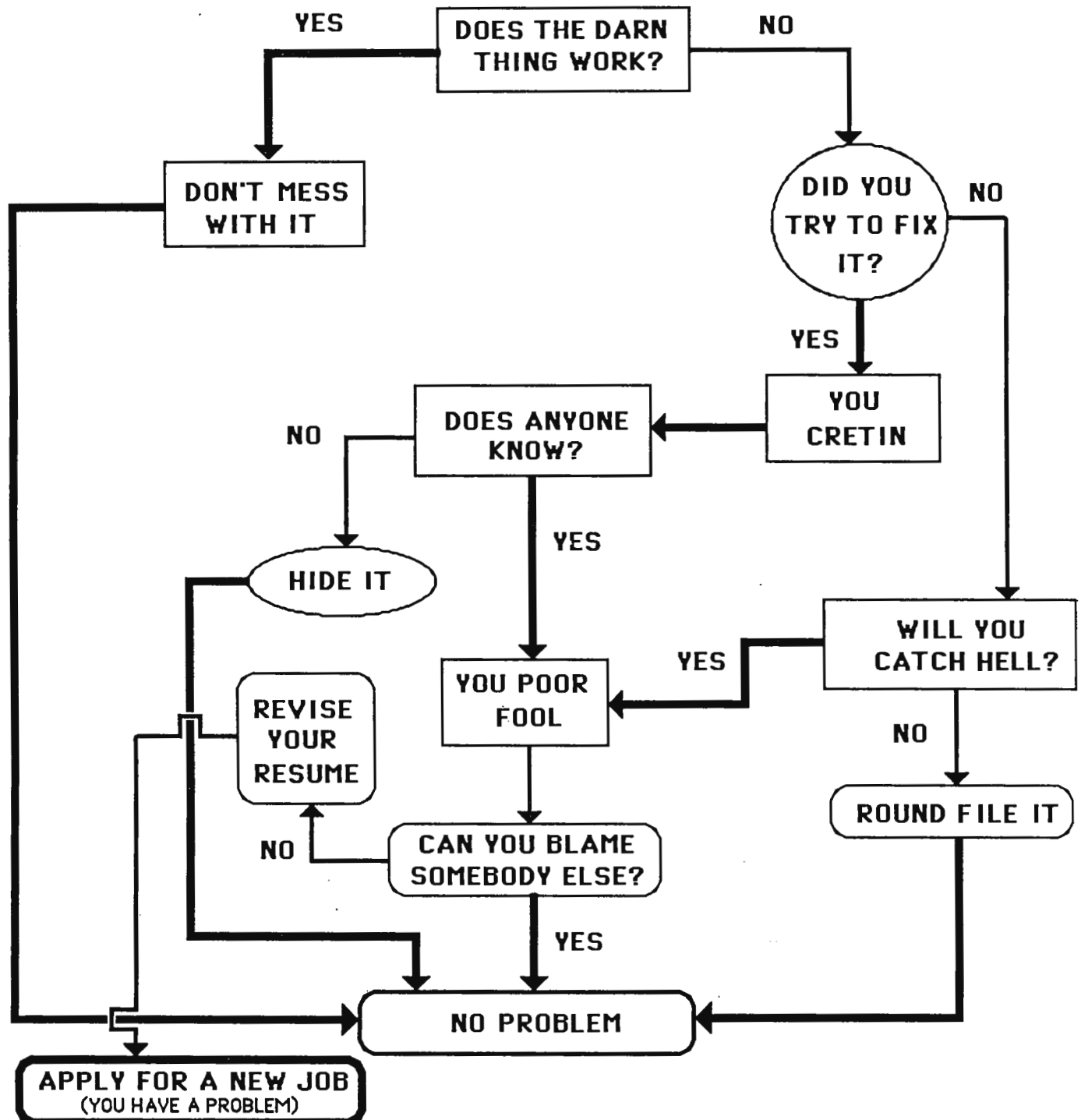
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# PROBLEM SOLVING FLOWSHEET



Out of Wm. F. Reynolds, by Gary E. Martin; the expurgated edition.

UNIVERSITY OF WASHINGTON  
DEPARTMENT OF CHEMISTRY  
SEATTLE, WASHINGTON 98195

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

August 22, 1988  
(received 8/25/88)

Dear Professor Shapiro,

Work in our laboratory has recently centered on improvements in our NOESY simulation program (NOESYSIM). NOESYSIM successfully models the diagonal asymmetry found in NOESY data sets acquired with short preparatory delays as noted last year in this newsletter. Using extensive NOESY simulation studies, we have now established that all of the deviations from diagonal symmetry are due to changes in the initial magnetization intensities (poster #112, 29<sup>th</sup> ENC). The signal matrix can therefore be given as

$$\mathbf{S} = [\exp(-\mathbf{R}\tau_m)] [\mathbf{S}]_{\tau_m=0}$$

where  $[\mathbf{S}]_{\tau_m=0}$  is a diagonal matrix (with elements  $S_{ij}^0$ ) that correspond to the driver function for all magnetization transfer during  $\tau_m$  and  $\mathbf{R}$  is the relaxation rate matrix. The individual signals can thus be accurately expressed as

$$S_{ij} = a_{ij} S_{ij}^0; \quad S_{ij} = a_{ij} S_{ij}^0 \neq a_{ji} S_{ji}^0 = S_{ji}$$

The mixing coefficients can be readily calculated from  $\mathbf{R}$  by matrix diagonalization procedures. At first, it might appear that the determination of  $S_{ij}$  at truncated preparatory delays would require numerical integration methods. We have found however, that  $S_{ij}$  can be evaluated from a 'control' matrix  $\mathbf{C}$

$$\mathbf{C} = \exp [-\mathbf{R} (\text{PD} + t_2)]$$

The summation of any row (or column) of  $\mathbf{C}$  yields the magnetization that is lost in a truncated preparatory delay experiment. Thus,

$$S_{ij}^0 = 1 - \sum_j c_{ij}$$

where  $c_{ij}$  are elements of  $\mathbf{C}$ . In the first version of NOESYSIM, signal matrices were indeed calculated by computationally-intensive numerical integration procedures. The procedure described above has now been incorporated into NOESYSIM and results in a 40-spin simulation requiring only ca. 1 second of cpu time (on a 10 MIPs cpu). We are now integrating NOESYSIM with conformation search routines of ALEX and QUANTA.

Additional improvements have involved the calculation of a best fit correlation time ( $\tau_c$ ) for a molecule based on analysis of an experimental NOESY data set. The ratios  $(S_{ij}/S_{ij})^{\text{calc}}$  vs.  $(S_{ij}/S_{ij})^{\text{obs}}$  are examined for a set of user-selected spin pairs whose crosspeak intensity is conformationally independent (*e.g.* geminal protons) and a best fit correlation time which minimizes the difference between the observed and calculated ratios is calculated. In addition, the residuals for all assigned cross peaks is calculated automatically for the normalized experimental and calculated data sets. This enhancement should be particularly valuable during conformational searches and constrained dynamics runs, generating a plot of the measure of fit as a function of the torsion angles scanned or the dynamic course.



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837 Arnold Drive Suite 600, Martinez, CA 94553  
Tel: (415) 229-3501 FAX (415) 229-1651

Another enhancement allows the theoretical NOESY spectrum to be displayed and plotted using a program which generates a 2-D real signal matrix in a format suitable for use in the program FTNMR (Hare Research). Chemical shifts as well as linewidths can be entered and the resulting dataset (an 'smx' file) can be manipulated and plotted (as contour or stacked plots) using the commands available in FTNMR. The figure below shows the simulated NOESY spectrum for a synthetic prostanoid whose NMR spectrum was fully assigned by 2-D COSY techniques. The top contour plot is a portion of the experimental NOESY spectrum and the bottom contour plot is a portion of the simulated NOESY spectrum.

These program enhancements will be made available to current and future subscribers of NOESYSIM in about two months once they have been fully debugged and made more user-friendly.

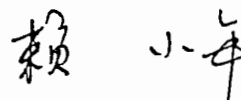
Yours sincerely,



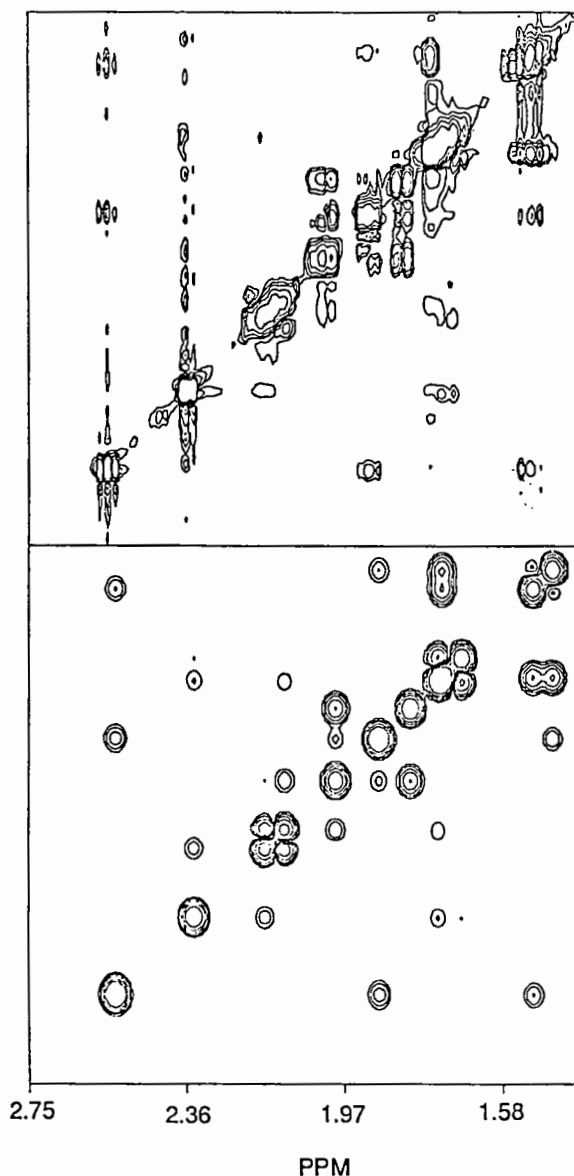
Niels H. Andersen



Thomas M. Marschner



Xiaonian Lai







Campus Chemical Instrument  
Center

176 West 19th Avenue  
Columbus, OH 43210-1173  
Phone 614-292-3446

8 August, 1988  
(received 8/15/88)

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

### 2-D Exchange and Matrix Diagonalization on an Aspect 3000

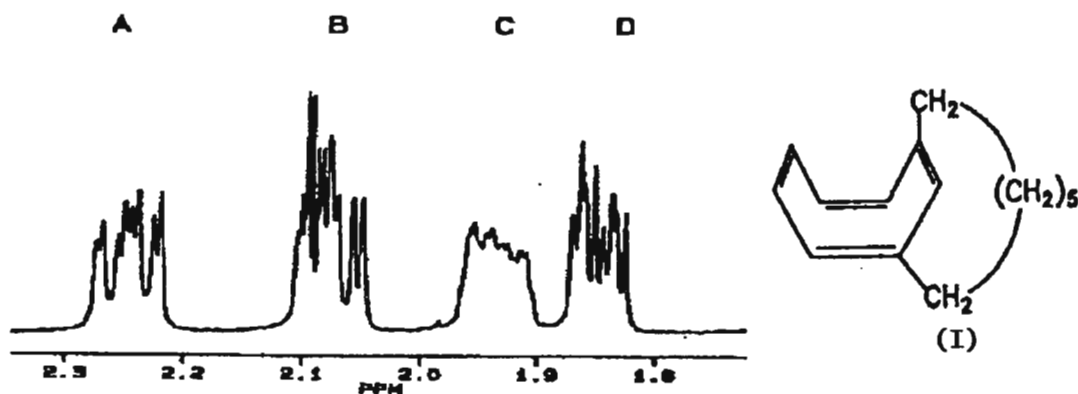
Dear Barry:

Recently I had occasion to study intramolecular exchange in 1,3-dialkyl substituted cyclooctatetraenes prepared in Dr. Leo Paquette's laboratory. One of these a COT bridged with a heptamethylene group is shown below (I). As the accompanying spectrum shows, the two important exchange mechanisms--tub-to-tub ring inversion and bond shifting-- are both slow at 303°K since the four allylic protons are nonequivalent. A CH correlation, as well as homodecoupling, confirmed that the methylene pairs are A/C and B/D. Although difficult to visualize without models (at least for me), the two exchange processes will act as follows:

Ring inversion       $H_A \leftrightarrow H_C$  and  $H_B \leftrightarrow H_D$

Bond shifting       $H_A \leftrightarrow H_B$  or  $H_D$  and  $H_C \leftrightarrow H_D$  or  $H_B$

I thought a 2-D chemical exchange experiment could give useful information concerning the exchange pathways as well as some quantitative rate constants for the two different processes.



Allylic region of (I) at 303° (500 MHz)

When the experiments were first performed (phase sensitive NOESY using TPPI as well as some strategies to suppress J-cross peaks), I did not have a program to calculate rate constants from 2-D EXSY data; however as details are in the literature (Refs 1 and 2), I thought I could put together a program (basically an eigenvalue problem) fairly quickly. I also decided to write the program in Pascal so the data could be processed on site using our ASPECT 3000. After a cursory review of some Pascal books, I could only find

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i.d.  $4.20 \pm 0.025\text{mm}$  (0.001 in.);  
camber  $\pm 0.03\text{mm}$  (0.0015 in.);  
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300 + .....\$1.90 ea.

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i.d.  $4.20 \pm 0.03\text{mm}$  (0.001 in.);  
camber  $\pm 0.04\text{mm}$  (0.002 in.);  
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camber  $\pm 0.07\text{mm}$  (0.003 in.);  
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i.d.  $8.76 \pm 0.025\text{mm}$  (0.001 in.);  
camber  $\pm 0.007\text{mm}$  (0.0003 in.).  
For additional length,  
add \$0.20 per cm (\$0.50/in.).

1-5 tubes...\$14.50 ea.  
6-25...\$13.75 ea.  
26 + .....\$12.95 ea.

##### No. 1005-P PRECISION for medium and high resln. NMR

Standard length: 178mm (7 inches);  
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i.d.  $8.76 \pm 0.025\text{mm}$  (0.001 in.);  
camber  $\pm 0.013\text{mm}$  (0.0005 in.).  
For additional length,  
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26 + .....\$9.00 ea.

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i.d.  $17.70 \pm 0.02\text{mm}$ ;  
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Date JULY 27 1982

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Title Asst. Teach.

Address INST. EXP. STATION

WINSTON-SALEM, NC 28698

Phone: 702-772-3311

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Wilma

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Type of NMR equipment used in the above evaluation EM-300 NMR

Date 12/2/83

Name L. WAYKOLE

Title GRA. INVENT

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Type of NMR equipment used in the above evaluation VARIAN EM-300

Date 11/3/82

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Title Asst. Prof.

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MURFREESBORO, TN 37132

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Type of NMR equipment used in the above evaluation VARIAN EM 360

Date 4/7/82

Name STEVEN MASLO

Occ. Assoc. Research

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IRVINE, CA 92714

Phone: (714)-957-7350

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Name L. Overman

Title Professor

Address Department of Chemistry

University of California

Irvine, CA 92717

Phone: 714-833-7156

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Type of NMR equipment used in the above evaluation VARIAN EM 360

Date

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Title Asst. Prof.

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# PERFORMANCE



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diagonalization routines for symmetric matrices. These routines would have been adequate for this special case, but, in general, the matrix which has to be diagonalized is not symmetrical once populations are taken into account. To be as general as possible, I decided to use a routine which diagonalized both real and complex matrices. Having at hand a FORTRAN version of the ALLMAT routine which is used in Binsch's line shape program, I succeeded in translating the program into Pascal. Unfortunately, I stumbled into a case in which the backsubstitution to calculate eigenvectors failed even though the eigenvalues were calculated correctly. That case is a split matrix with degenerate eigenvalues, e.g.

$$\begin{bmatrix} 3 & 1 & 0 & 0 \\ 1 & 3 & 0 & 0 \\ 0 & 0 & 3 & 1 \\ 0 & 0 & 1 & 3 \end{bmatrix} \quad \text{or not as visually obvious} \quad \begin{bmatrix} 3 & 0 & 1 & 0 \\ 0 & 3 & 0 & 1 \\ 1 & 0 & 3 & 0 \\ 0 & 1 & 0 & 3 \end{bmatrix}$$

(The matrix on the right is transformed to that on the left when the matrix is converted to an upper triangular (Hessenberg) matrix.)

While not ruling out a programming error on my part, I decided to try a different approach and translated COMLR2, which can be found in EISPACE. This routine accumulates the eigenvectors during the diagonalization, thereby avoiding the need for backsubstitution. Finally I had a working program which can be used to calculate rate constants and which can also be used in reverse to calculate theoretical intensities starting with rate constants, T1's, and populations. Note: The difficulty I had with ALLMAT should not be a problem in line shape calculations.

When I finally was able to extract rate data from the 2-D EXSY experiments, the following results were obtained (mixing time of 0.5 sec):

Temp °K	k (ring inversion)	k(bond shifting)
303	0.6 sec <sup>-1</sup>	-----
318	1.6	0.16
333	indeterminate	$\tau_m$ set too long

The last result(?) confirms how useful it is to be able to compute theoretical intensities to select an optimum mixing time. This version of the program does not include cross relaxation which might cause the value for ring inversion to be underestimated. These preliminary results also suggest that bond shifting exchanges H<sub>A</sub> and H<sub>D</sub>.

For readers interested in this subject: Depending on how populations are factored into the area matrix, different authors get rate matrices which are transposed. I have followed Abel's convention in that element [1,2] of the rate matrix corresponds to the rate constant k<sub>12</sub> for (1) → (2). A PASCOM version of this program has been submitted to the Bruker user group ABACUS.

Please credit this to Alan Marshall's account.

Sincerely,

*Chuck*

Charles E. Cottrell, Ph.D.  
NMR LAB Manager

CEC/kc

1. E. W. Abel, et al., J. Mag. Res., 70, 34(1986).
2. C. L. Perrin and R. K. Giper, J. Am. Chem. Soc., 106, 4036(1984).

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8/ 4/ 88

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

Dear Dr. Shapiro,

For quite a while, I have wanted to earn the right to a subscription to the TAMU Newsletter by submission of original work pertaining to NMR. This posed a problem, as I am not a practicing scientist, but a humble sales rep.

During my travels, I met a mass spectroscopist who claimed that the uniquely unorthodox personality traits of the NMR community were attributable to "too many Teslas." However, my friend, Dr. Joanne Bonesteel, informs me that it is merely the result of living in a rotating frame.

Therefore, let me suggest that you devote a fraction of the TAMU newsletter to the human side of NMR-- a page which might be titled  
"Life in the Rotating Frame."

As you can see, I've included a few examples. These are originals, so please handle them carefully. Dr. Shapiro, I hope that you like this cockamamie idea, and that you will credit Merck Isotopes for subscription rights (although you shouldn't blame them for this nonsense, which is entirely my own fault).

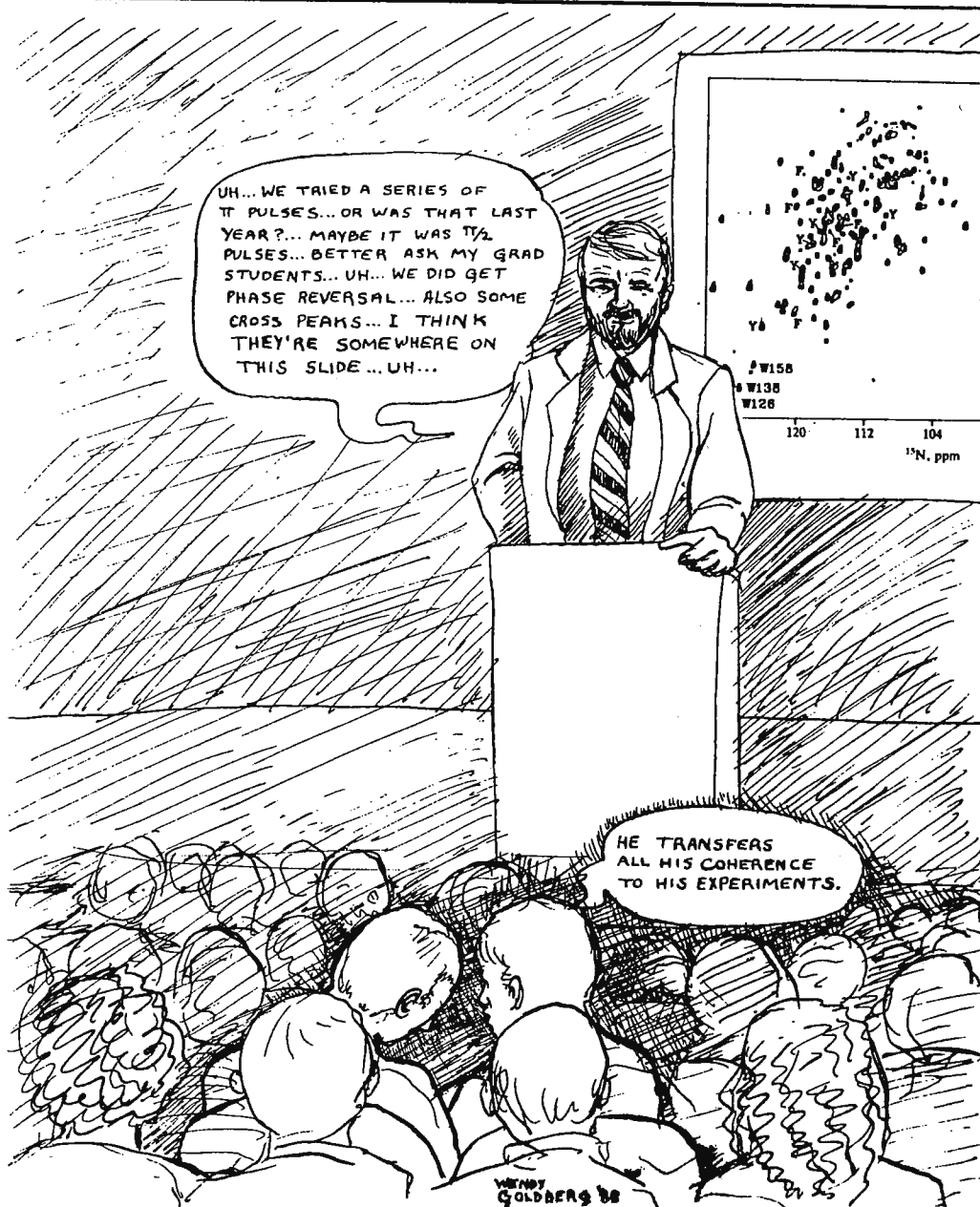
With any luck, the idea will catch on, and the rest of the NMR community will continue the column.

Hope you're having fun in the sun.

Sincerely,

  
Wendy Goldberg

## LIFE IN THE ROTATING FRAME



Now and then, perhaps a bit of horsing around is not amiss. It would be interesting if others would also attempt to bring a ray of sunshine to a Newsletter grown a trifle stodgy after 30 years. Surely someone will rise to this challenge. Such contributions to culture are, of course, 'not for credit' to the donor's Newsletter account. Permission to use items submitted in the Newsletter will be assumed, on a non-exclusive basis.

B.L.S.



# NMR

## NEWSLETTER

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\* \* \* \* \*

### Newsletter Subscription and Sponsorship Renewals

Invoices for the 1988-89 Newsletter year have been mailed out over a month ago to all **Subscribers**, and all of the Newsletter **Sponsor** organizations and **Advertisers** have also been contacted about renewing their annual support of this self-supporting publication. If you have not received an invoice or a letter by the time you read this notice, please let me know without delay.

It will be greatly appreciated if you will see that these invoices are processed promptly, in order that the costs of operating the Newsletter can be 'contained'. Fiscal considerations require that **Subscription payment must be received** (or clear indication given me that payment is in the works) **by October 15, 1988** if your Newsletter mailings are to continue without interruption. Many payments have already been received, and I thank those responsible for their promptness.

Several of our **Sponsors** have also responded as of this date, and I hope those yet to do so will be able to indicate their intention to renew their vital support of the Newsletter before long. The Newsletter's financial circumstances are always marginal, and this is more true than ever this year. Significantly increased income is needed, and we hope that our loyal **Sponsors** and **Advertisers** will be able to share with the **Subscribers** the task of meeting the ever increasing costs of the Newsletter.

B.L.S.  
10 August 1988

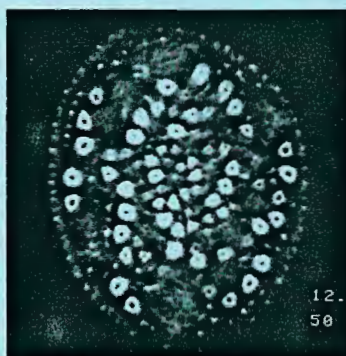
# CSI 2T Applications

## Shielded Gradients and NMR Microscopy

In spin warp imaging, there is a trade-off between minimum TE and maximum resolution. Even if rise and fall times were zero and phase encoding occurred during the entire echo delay, a  $\pm 2$  Gauss/cm gradient range and a TE of 2 msec would provide best case resolution of 0.32 mm. This translates to a 7 cm field of view in a  $256 \times 256$  matrix. To improve resolution by a factor of 10, TE may be increased by a factor of 10 (which is not acceptable in a sample with short T2 values) or gradient strength may be increased by a factor of 10. The long echo times required for T2 weighted images create an undesired loss of signal in many non-T2 weighted image experiments. These effects, however, are tolerable at 2 Gauss/cm for resolution at the 100-200 micron level.

Clearly, added signal that would be available with a shorter TE would be useful. The current practical limits of high signal-to-noise NMR micro imaging are greatly reduced by high strength shielded gradients. A 50 micron resolution image of an Agapanthus bud is shown in Figure 1. Unlike very high field ( $> 7$  Tesla) micro NMR imaging, magnetic susceptibility effects at 2T do not compromise the 50 micron digital resolution obtained during these gradient strengths.

In a second example, (Figs. 2 and 3), 25 micron resolution is achieved in a small phantom by using a moderate access (5 cm) rf coil. The phantom consists of seven small capillary pipets in a 5 mm NMR tube. Data was collected as a  $32 \times 256 \times 256$  DEFT data set.



**Fig. 1**—Agapanthus bud  
Matrix  $256 \times 256$ , TR 200  
Slice 2 mm, TE 30  
FOV 12.8 mm, NEX 4,  
45° Tip Angle DEFT  
Sequence



**Fig. 2**—16 contiguous 1 mm  
slices  
FOV 6.4 mm, NEX 4.  
TR 150 msec, Field Strength  
2T, TE 14 msec



**Fig. 3**—Expanded view of  
four of the 16 slices shown  
in Fig. 2.



**GE NMR Instruments**

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# JEOL'S GSX-FT NMR Systems

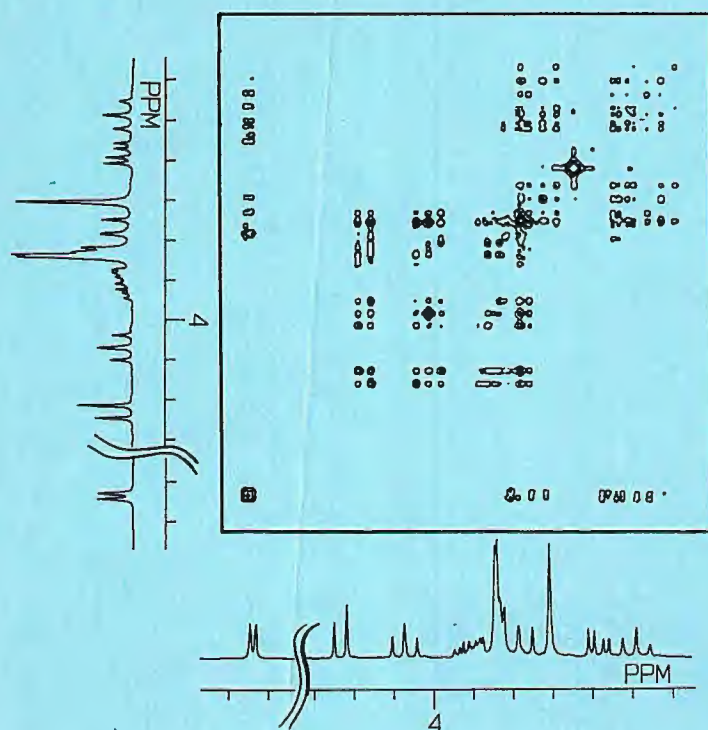
## Application: Pulse Programming

The GSX pulse programmer was designed with sufficient flexibility and range to do the most sophisticated routines you see in the current literature. While these routines may be of no interest for your present NMR applications, the next issue may have just the perfect experiment. As an example of these capabilities, consider HOHAHA.\*

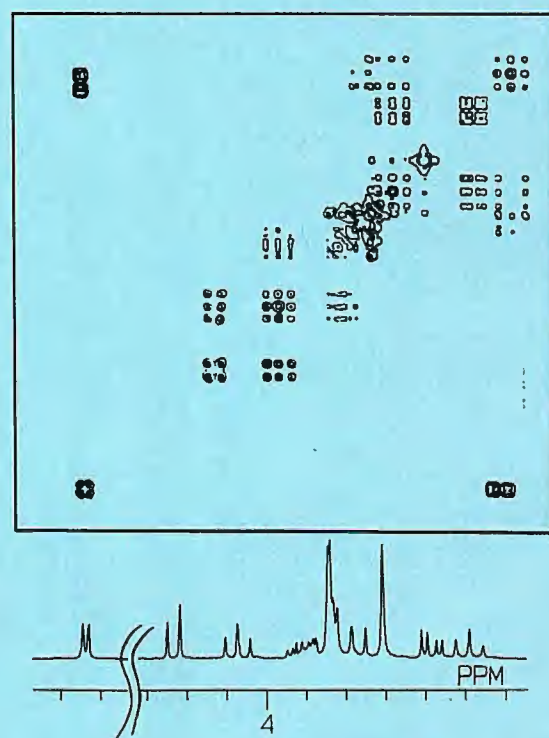
The HOHAHA experiments which use MLEV-17 for spin locking are very good for providing connectivity, especially in small molecules which produce poor RELAY experimental results. The spin locking allows coherence transfer which can be controlled by the mixing times. Directly coupled protons can be detected with short mixing times (20 ms) while longer mixing times result in relayed coherence transfers — many times with more sensitivity than RELAY experiments.

The data below are from a wide bore GSX-270 and compares the normal COSY experiment using 3 mg of sucrose in D<sub>2</sub>O with the HOHAHA experiment run on the same sample. The spin locking used for the HOHAHA produces relayed coherencies which are shown by the additional cross peaks in the contour plot.

HOHAHA DATA



COSY DATA



\*Ad Bax and Donald G. Davis, *J. Mag. Res.*, 65, 355 (1985).