TEXAS A&M UNIVERSITY
NMR NEWSLETTER

No. 391

April 1991

Continued on page 2

TABLE 1 DEUTERATED SOLVENTS

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D-11	[illegible]	[illegible]COOD	[illegible]	1.1[illegible]	[illegible]	[illegible]	0.551 (32)
D-120	[illegible]		[illegible]				
D-13	Acetone-d_6	CD_3COCD_3	99.[illegible]%	0.8[illegible]	[illegible]94	[illegible]7	0.460 (20)
D-121	Aceonte-d_6 + 1% TMS		99.8%				
D-129	[illegible]						
D-14	[illegible]						[illegible]543 (20)
D-21	[illegible]						[illegible]0.611
D-122	[illegible]						
D-130	[illegible]						
D-28	Choloroform-d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-31	Chloroform-d + 1% TMS		99.8%				

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WCV-XL ([illegible])	[illegible]	[illegible]	Gridded-Two Color
WCV-XLFT-[illegible]	[illegible]	XL-100 ([illegible] and FT)	Gridded-Two Color
WCV-XL-200	11" X 26"	XL-200, XL-300, XL-400	Gridded-Two Color
[illegible]	[illegible]	[illegible]	[illegible]
WCV-20 (CFT-20)	11" X 16 3/4"	CFT-20, FT-80, FT-80A	Gridded-Two Color
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FORTHCOMING NMR MEETINGS

Second Annual Workshop on Magnetic Resonance Imaging of Materials, Mass. General Hospital NMR Center, Charlestown, MA, , **May 13 - 14, 1991**; See Newsletter 388, 43.

Fifth Washington University-ENI/Emerson Electric Co., Symposium on NMR, St. Louis, Missouri, **May 20, 1991**; See Newsletter 391, 44.

Contrast-Enhanced Magnetic Resonance, a workshop of the Society of Magnetic Resonance in Medicine, Napa, California, **May 23-25, 1991**; Contact: S.M.R.M., 1918 University Ave., Suite 3C, Berkeley, CA 94704; (415) 841-1899, FAX: (415) 841-2340; See Newsletter 391, 42.

Eleventh Delaware NMR Symposium, Univ. of Delaware, Newark, DE, **June 4, 1991** See Newsletter 390, 35.

Tenth International Meeting on NMR Spectroscopy, St. Andrews, Scotland, **July 8-12, 1991**; Contact: Dr. John F. Gibson, Secretary (Scientific), The Royal Society of Chemistry, Burlington House, London W1V 0BN, England; See Newsletter 387, 69.

Gordon Research Conference on Magnetic Resonance, Brewster Academy, Wolfeboro, NH, **July 15-19, 1991**; Chairman: R. Griffin; Information from Dr. A. M. Cruickshank, Gordon Research Center, Univ. of Rhode Island, Kingston, RI 02881-0801; Tel.: (401) 783-4011 or -3372; FAX (401) 783-7644.

Tenth Annual Scientific Meeting and Exhibition, Society of Magnetic Resonance in Medicine, San Francisco, **August 10-16, 1991**; Contact: S.M.R.M., 1918 University Ave., Suite 3C, Berkeley, CA 94704; (415) 841-1899, FAX: (415) 841-2340; See Newsletter 391, 55.

International Conference on NMR Microscopy, Heidelberg, Germany, **September 16 - 19, 1991**; See Newsletter 385, 28.

1991 Joint Meeting FACSS/Pacific Conference, Anaheim, California, **October 6-11, 1991**; NMR/EPR Program Section Chairman: Prof. Cecil R. Dybowski, Chemistry Dept., Univ. of Delaware, Newark, DE 19716. Contact: FACSS, P.O. Box 278, Manhattan, KS 66502-0003.

Eighth Australian NMR Conference, Lorne, Victoria, Australia, **February 2-6, 1992**; See Newsletter 391, 38.

Eleventh Annual Scientific Meeting and Exhibition, Society of Magnetic Resonance in Medicine, Berlin, Germany, **August 8-14, 1992**; Contact: S.M.R.M., 1918 University Ave., Suite 3C, Berkeley, CA 94704; (415) 841-1899, FAX: (415) 841-2340.

Additional listings of meetings, etc., are invited.

Table of Contents, cont'd.

* * * *

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If the mailing label on your envelope of this issue is adorned with a large red dot or circle: this decoration means that you will not be mailed any more issues until a technical contribution has been received by me.

Page Length ~~Request~~ Instruction

Attention overseas subscribers: If you must use paper which is longer that 11", *please* take care that all material (including signatures, addresses - everything!) ends no more than 10" from the top of each of your pages. It is costly to make reductions, and henceforth I reserve the right to chop the excess length off any page, no matter what the result. Beware of the dreaded guillotine! Your cooperation in this matter will be greatly appreciated. Thank you.

All Newsletter Correspondence
Should Be Addressed To:

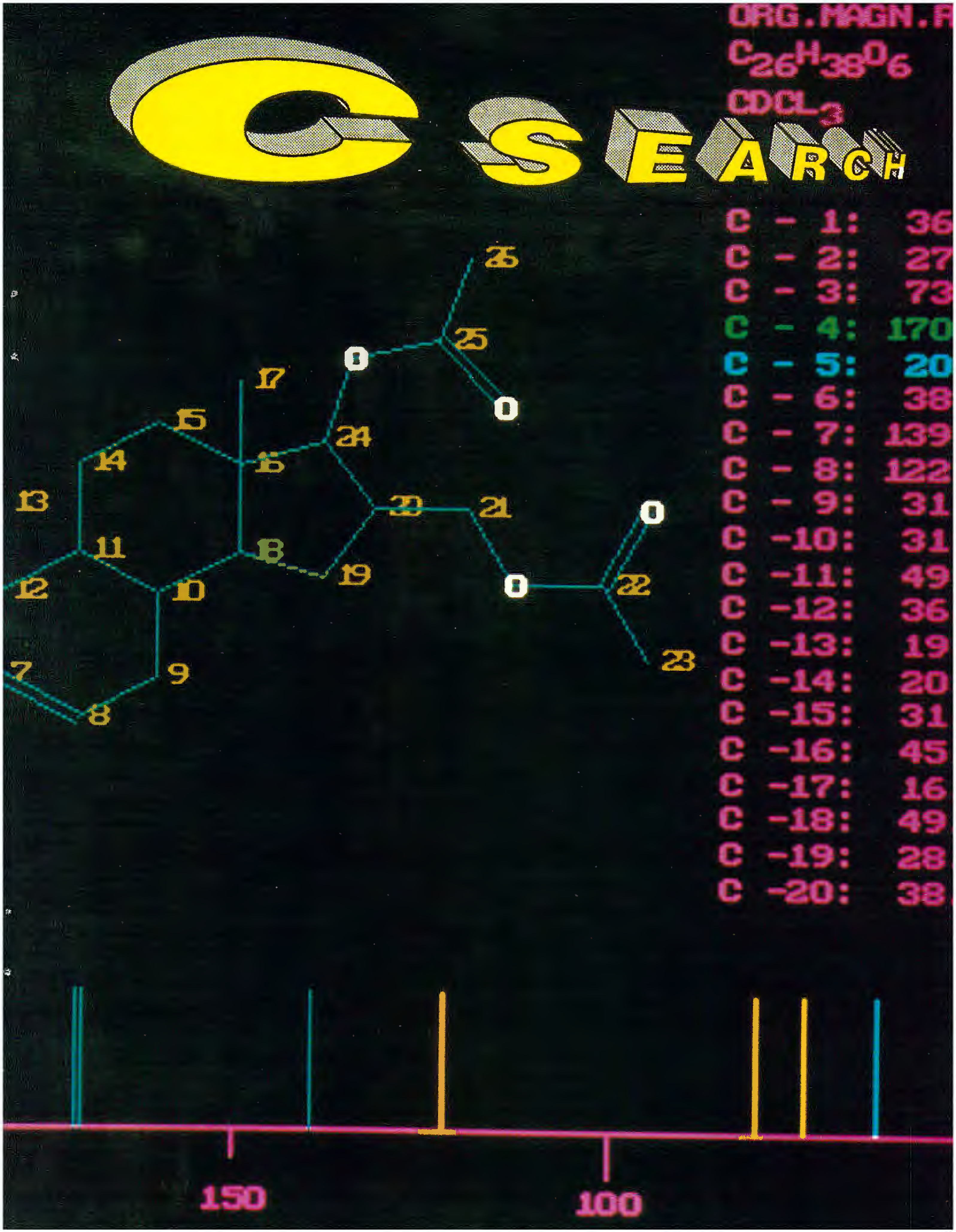
Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303, U.S.A.

(415) 493-5971

DEADLINE DATES

No. 393 (June)-------------------- 17 May 1991
No. 394 (July)-------------------- 21 June 1991
No. 395 (August)----------------- 19 July 1991
No. 396 (September)-------- 16 August 1991

* * * * *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Dr. Bernard L. Shapiro
TAMU NMR News Letter
966 Elsinore Ct.
Palo Alto, CA 94303

Determination of Mole Fraction of free Mn^{2+} Ions in the Presence of Mn(III)$TPPS_4$ by the T_1/T_2 Ratio of Solvent Water Protons

(received 2/19/91)

Dear Dr. Shapiro:

Water soluble manganese(III) porphyrins are prepared by reacting a porphyrin with an excess of manganese salt, and the product can be a mixture of the manganese(III) porphyrin and unreacted free Mn^{2+} ions. We are interested in the relaxation rates of water protons in aqueous solutions containing manganese(III) porphyrins, and the presence of additional free Mn^{2+} ions will cause the interpretation of the relaxation rates to be inaccurate. This report describes a simple NMR experiment that was developed to detect and quantify free Mn^{2+} ions in the presence of manganese(III) porphyrins.

The T_1/T_2 ratio is close to unity at all magnetic field strengths (1) for solutions containing only manganese(III) porphyrins. However, the ratio T_1/T_2 becomes much larger than unity at high ($\geq$90 MHz) magnetic field strengths for solutions containing only free Mn^{2+} ions. The larger value of this ratio for solutions of free Mn^{2+} ions is a result of a contact, or hyperfine, interaction between the manganese and the protons of the bound water molecules that causes $1/T_2$ to be much larger than $1/T_1$ (1). Therefore, for solutions containing both free Mn^{2+} ions and manganese(III) porphyrins, the T_1/T_2 ratio of the solvent water protons at high magnetic fields can be used to quantify the mole fraction of both manganese species. Although only the quantitation of free Mn^{2+} ions in the presence of manganese(III) tetraphenylsulfonyl porphyrin [Mn(III)$TPPS_4$] in aqueous solution is demonstrated in this report, the results apply to other manganese porphyrins and chelated manganese(II) ions as well, because the contact interaction is unique to free Mn^{2+} ions (1).

For a solution containing both free Mn^{2+} ions and Mn(III)$TPPS_4$, the solvent water molecules experience three different environments: the inner coordination sphere of the free Mn^{2+} ions, the inner coordination sphere of the Mn(III) porphyrins, and bulk water. Because of rapid exchange, a single water molecule will sample each of the three environments many times during a time interval of T_i (i = 1, 2), and the measured relaxation rate $1/T_i$ will be a weighted average of all the $1/T_i$ rates characteristic of each environment (2):

$$\frac{1}{T_i} = \frac{1}{T_{1W}} + \frac{6[Mn^{2+}]}{55.5}\frac{1}{T_{iMF}} + \frac{2[MnP]}{55.5}\frac{1}{T_{iMB}} \qquad \text{for } i = 1, 2 \qquad (1)$$

where $1/T_{iW}$ are the relaxation rates of free water molecules, and $1/T_{iF}$ and $1/T_{iB}$ are the relaxation rates of water molecules bound in the inner coordination sphere of free Mn^{2+} ions and Mn(III) porphyrins respectively. The brackets denote molar concentrations of the particular manganese species; 6 is the number of water molecules in the inner coordination sphere of free Mn^{2+}ions; 2, the number in Mn(III)$TPPS_4$.

To quantify the relative amounts of free Mn^{2+} ions and Mn(III)$TPPS_4$ in solution, the T_1/T_2 ratio must be dependent on only the mole fraction of either manganese species. Relaxivities, R_i, which are independent of concentration, are defined for solutions containing only free Mn^{2+} ions or only Mn(III)$TPPS_4$:

$$R_i = \frac{\frac{1}{T_{iP}}}{[Mn]}, \qquad \text{where } \frac{1}{T_{iP}} = \frac{1}{T_i} - \frac{1}{T_{iW}} \qquad \text{for } i = 1, 2 \qquad (2)$$

where [Mn] is the concentration of either free Mn^{2+} ions or Mn(III)$TPPS_4$.

For solutions containing both free Mn^{2+} ions and Mn(III)$TPPS_4$ porphyrins, the T_{1P}/T_{2P} ratio, in terms of the mole fraction of free Mn^{2+} ions X_F, is given by:

$$\frac{T_{1P}}{T_{2P}} = \frac{X_F(R_{2F} - R_{2B}) + R_{2B}}{X_F(R_{1F} - R_{1B}) + R_{1B}} \quad (3)$$

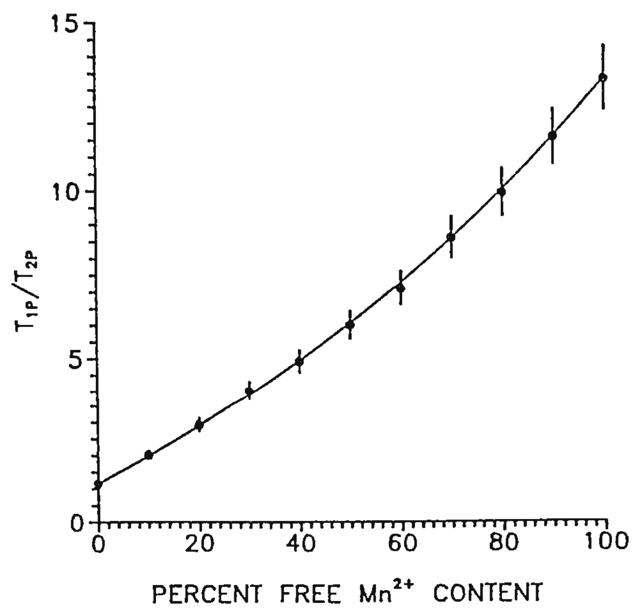
where R_{iF} and R_{iB} are the relaxivities of solutions containing only free Mn^{2+} ions and only $MnTPPS_4$ respectively.

The relaxivities of both free Mn^{2+} ions and Mn(III)$TPPS_4$, and $1/T_i$ for free water were measured at 27°C and at 90 MHz. Based on these six values, the solid line shown in Figure 1 was calculated for various mole fractions of free Mn^{2+} ions via Equation (3); it is not a best-fit line but rather a calibration curve. Solutions of known free Mn^{2+} ions and Mn(III)$TPPS_4$ composition were prepared, the experimental T_{1P}/T_{2P} ratios were obtained, and the results are shown as the data points in Figure 1. The accuracy in the determination of the mole fractions by this method may appear somewhat surprising, because the accuracy in a T_1 or a T_2 measurement is usually limited to 10% and 15% respectively, and these errors would be magnified when a ratio is taken. However, regardless of whether the absolute magnitudes obtained for T_1 or T_2 are correct, the reproducibilities of our experimental T_{1P}/T_{2P} ratio are very good (within ±7.3%), and therefore the precision rather than the accuracy accounts for the close agreement between the measured and predicted values.

Kenneth E. Kellar   Natalie Foster   James E. Roberts   William R. Anderson

1. Koenig, S.H. ; Brown III, R.D. *Magn. Reson. Med.* 1984, 1, 478.
2. Koenig, S.H. ; Brown III, R.D. *J. Magn. Reson.* 1985, 61, 426.

Figure 1. The data points display the T_{1P}/T_{2P} ratios measured at 90 MHz and 27°C for solutions containing a given mole fraction of free Mn^{2+} ions and Mn(III)$TPPS_4$. The solid calibration curve calculated from Equation (3) is also shown. The total concentration of both manganese species was 1 mM for all data points.



The University of Akron
Department of Chemistry (216) 972-7372
Akron, Ohio 44325

January 29, 1991 (received 2/21/91)

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

Title: Digital Filtering to Improve 2D-INADEQUATE Spectra

Dear Barry,

The 2D-INADEQUATE experiment would undoubtedly be the most powerful of 2D-NMR experiments if it were not for its inherently poor sensitivity. We have continued to play with applications of Principal Component Analysis (PCA, J. Magn. Reson. 88, 320 (1990)) to improve 2D-NMR spectra, and have found that it is very good at removing a number of commonly found artifacts in 2D-INADEQUATE spectra.

The enclosed Figure shows the spectra obtained from Lasalocid before (a) and after (b) removal of one principal component, PC. There is considerable improvement in the spectrum after PCA, in effect providing an improvement of the signal-to-noise. Note that a very prominent artifact from uncancelled single quantum coherence of the solvent resonance is removed to reveal the second half of a pair of double quantum coherence correlations. Unlike COSY spectra which require a larger number of iterations to remove the first 10–20 PC's, removal of only 1 or 2 PC's from 2D-INADEQUATE spectra produce the most noticeable improvement. Calculation times are dependent on the size of the 2D matrix, but are generally only a fraction of the 2D-FT times.

Best regards,

James K. Hardy Vincent E. Litman Peter L. Rinaldi

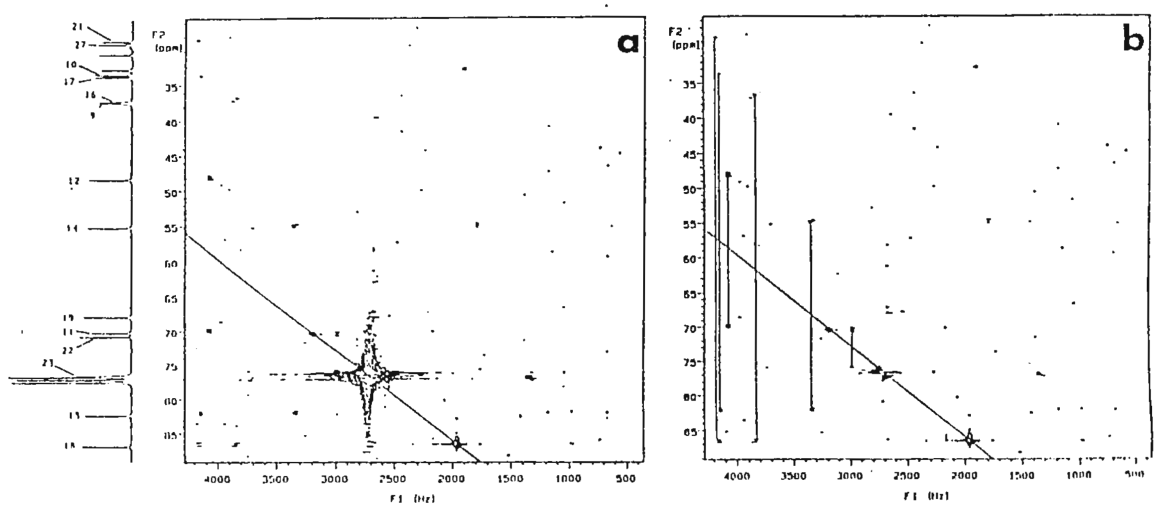


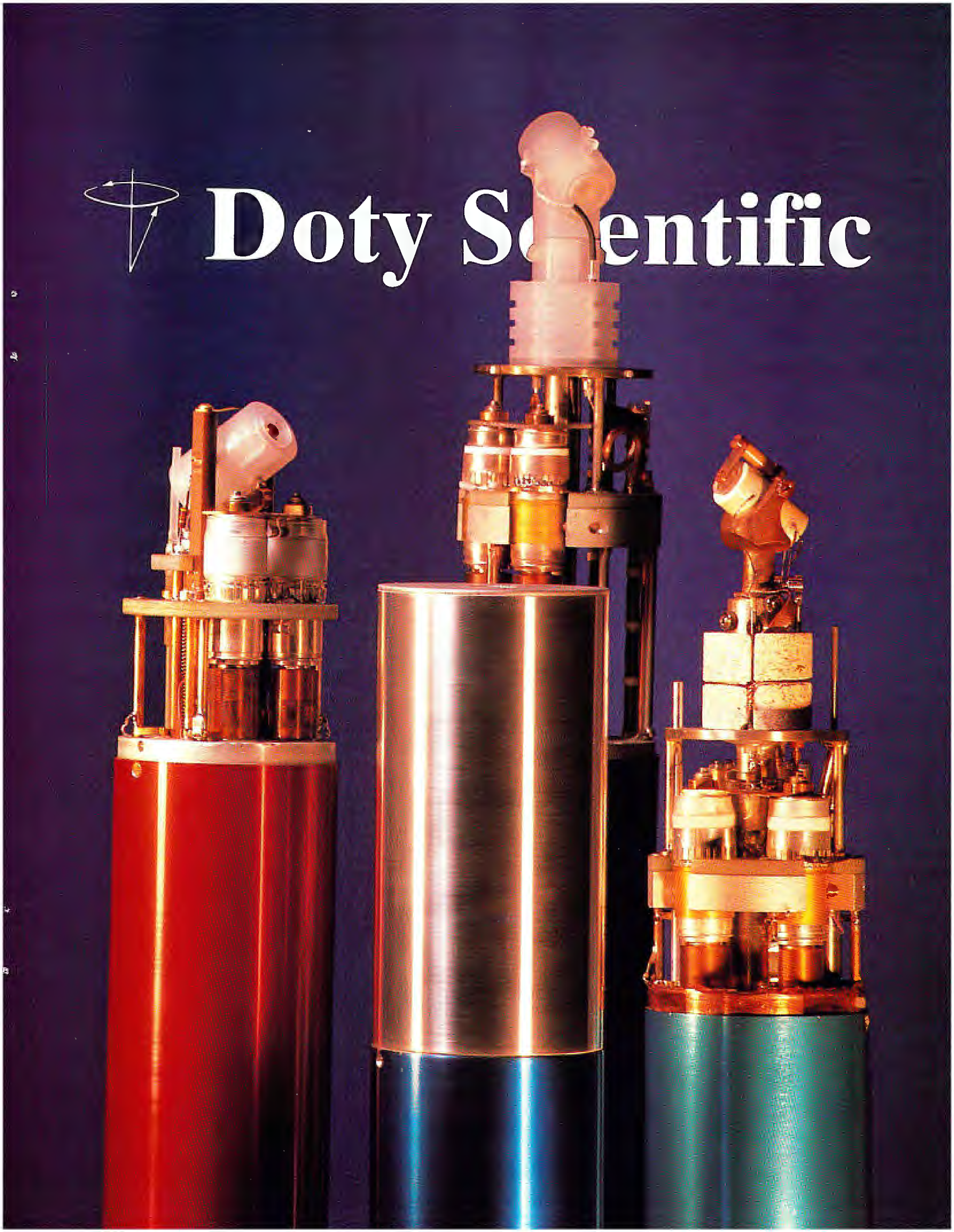
Figure 1. Sample region from the 2D-INADEQUATE spectrum of Lasalocid (**1**): (a) before PCA, and (b) after PCA digital filtration. The spectra were obtained from 700mg of the sodium salt of **1** in 2ml of $CDCl_3$ doped with 12mg of $Cr(acac)_3$ as a relaxation agent, contained in a 10mm tube. Experiments were performed at 75.429 MHz on a Varian VXR–300 nmr spectrometer. Absolute value data were collected at ambient temperature without sample spinning; delays were optimized for J_{CC}= 40 Hz and a total of 192 fid's were acquired with 512 transients and 4 dummy pulses, 20 μs 90° pulse width, 3 s relaxation delay, 0.115 s acquisition time (4096 points) and 17793.6 Hz spectral windows in f_1 and f_2. The data was processed using VNMR software on a Sun-SPARCstation–1 using zero filling to 8196 X 1024 and 1Hz exponential linebroadening in both dimensions. PCA was performed on the 4096 X 512 display file. The first principal component, accounting for 40.1% of the variance, was calculated and subtracted from the spectrum in Figure 1a to produce the spectrum in Figure 1b (PCA computation time 5 minutes).

POSTDOCTORAL POSITION

I currently have a postdoctoral position open in my laboratory. Projects include development of new methods for rapid collection of 3D–NMR data, development of new methods for digital filtration of 2D–NMR data, development of new 2D– and 3D–NMR methods for characterizing high molecular weight molecules in solution, and development of 2D–NMR techniques to study substrate binding. We are applying these methods to the characterization of new synthetic polymers and the investigation of substrate binding to biomolecules. Equipment available includes Gemini–300, VXR–300 and XL–400 widebore liquids and 200 MHz widebore solids spectrometers. These instruments are linked via an Ethernet network to ca. 9 Sun and Silicon Graphics workstations for offline data processing and molecular modeling.

If you are interested in this position contact me and send a CV and 3 reference letters.

Peter Rinaldi
Department of Chemistry
The University of Akron
Akron, OH 44325–3601
216–375–5990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^{15}N CSA Spectra of Select Monomers and Polymers

(received 2/25/91)

Dear Dr. Shapiro:

Please forgive the delay in sending in a technical contribution. We are in the final stages of moving our two existing NMR systems as well as installing two new spectrometers in our new polymer science research center. This is a 3-story 86,000 square foot facility with state-of-the-art labs containing $6 million in new polymer analysis equipment. Our only comment about the move is a warning to owners of older spectrometers: older instruments, like older people, get very cranky if you make them get up from a comfortable position.

One of our major areas of interest is the characterization of rigid-rod and nylon materials via solid-state ^{15}N NMR spectroscopy. Although we have utilized CP/MAS and MAS/HPD techniques to obtain information on the amorphous, interfacial, and crystalline regions of a variety of nylons (*J. Amer. Chem. Soc.*, **1990**, *112*, 669), we have not been able to use the CSA patterns from these materials due to the low natural abundance of the isotope. Recently, we synthesized a series of isotopically labeled monomers and polymers and initiated a study of their CSA spectra in order to obtain additional information about the nature of the bonding about the amide and imide linkages. Given on the next page are ^{15}N CSA spectra for a series of substituted bisphthalimides and a polyimide film. From a qualitative perspective, a shift in the σ_{22} tensor is observed as the hydrogen is replaced by benzyl and alkyl groups, respectively. This is not totally unexpected, since this tensor has been postulated to be more sensitive to changes in bonding and conformation than σ_{11} or σ_{33} (*Macromolecules*, **1989**, *22*, 2860). Also, it is evident that the overall axial symmetry of the CSA powder pattern is preserved for the spectra b-d and is lost in the polymer (spectrum a). We are beginning to analyze these spectra along with several doubly-labeled materials (^{15}N-^{13}C) using Dr. Terry Oas's simulation program (*J. Magn. Reson.*, **1988**, *78*, 408), which he has graciously given to us. We will report the preliminary results of these studies in a later issue.

Sincerely,

W. L. Jarrett   C. Greg Johnson   Lon J. Mathias

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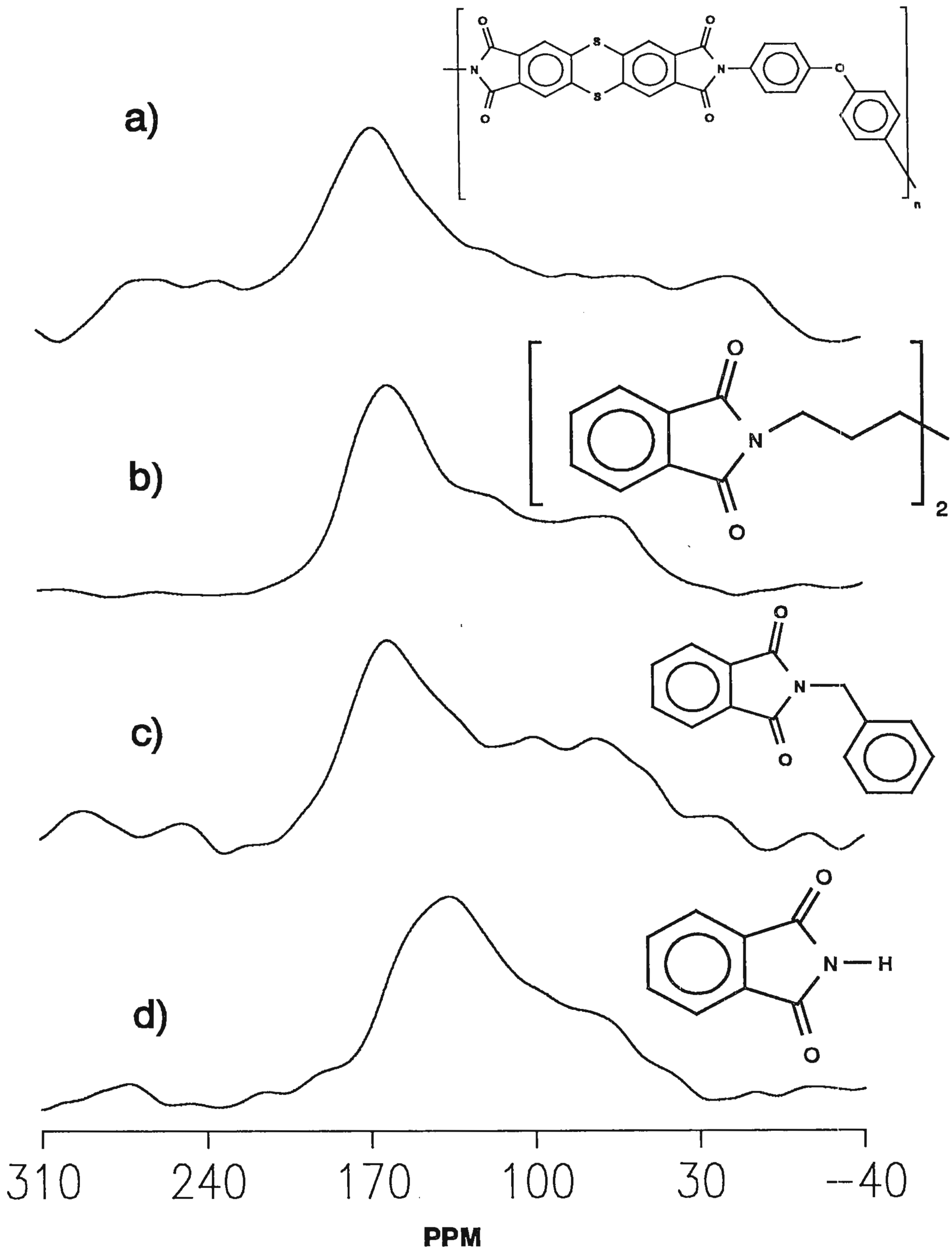
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Dr. B.L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
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February 11, 1991
(received 2/25/91)

NMR Parameter Estimation Using Bayesian Probability Theory.
("To FT or Not to FT?" That Is the Question.)

Dear Barry:

We are currently investigating the use of Bayesian probability theory as an alternative to the standard discrete Fourier transform (DFT) analysis of NMR time-domain FID data. While the theory behind this approach has recently been published (1), to our knowledge no direct, rigorous comparison between Bayesian methods and the DFT methods has been reported. In lieu of this, we would like to share some preliminary results that help compare/contrast the Bayesian methodology to the standard DFT methods currently available on our Varian VXR 500 NMR spectrometer (software version 3.1).

The initial question posed at the beginning of our studies was straight forward: How precisely do Bayesian and DFT methods provide estimates of the frequency and the signal amplitude for a single frequency NMR signal as a function of the signal-to-noise (S/N) ratio of the FID data? The two analysis procedures were compared using a high time-domain S/N (*e.g.*, S/N = 4,000) and greatly digitized (48 K data points over 5 T_2^*) ^{1}H NMR FID data set containing only one frequency (*e.g.*, residual HOD resonance of D_2O). Estimates of the off-resonance frequency and signal amplitude for the NMR signal were made on this FID data set and on combined data sets which resulted from the addition of variable amounts of computer-generated white Gaussian noise to the FID data. If we accept the parameter estimates obtained for the "noiseless" FID data as the true parameter values (*i.e.*, frequency = -1000 Hz; normalized signal amplitude = 100), then any deviation or scatter from these values estimated from the combined data sets (*i.e.*, FID + noise) should reflect uncertainty in the analytical procedures introduced by the addition of the noise.

The experimental results are shown in the accompanying Figure and clearly indicate that the Bayesian analysis provides a much higher degree of precision for both the frequency and the signal amplitude estimates than the DFT procedures, especially at low S/N levels. In fact, the Bayesian analysis yields reasonable estimates even when S/N levels are well below the threshold where the DFT analysis seems to breaks down completely. We find these results to be extremely encouraging and believe they raise notable questions concerning the traditional (and generally unquestioned) use of a DFT as a means with which to analyze time-domain NMR FID data.

We are extending our studies by examining the effects that truncation of the NMR FID data and use of prior knowledge of the phase and signal decay rate (*i.e.*, use of matched weighting filter) have on the analysis procedures. While completion of a rigorous comparison between the two methods remains in progress, we anticipate that Bayesian methods will play a significant role as an alternative, non-Fourier NMR data analysis technique.

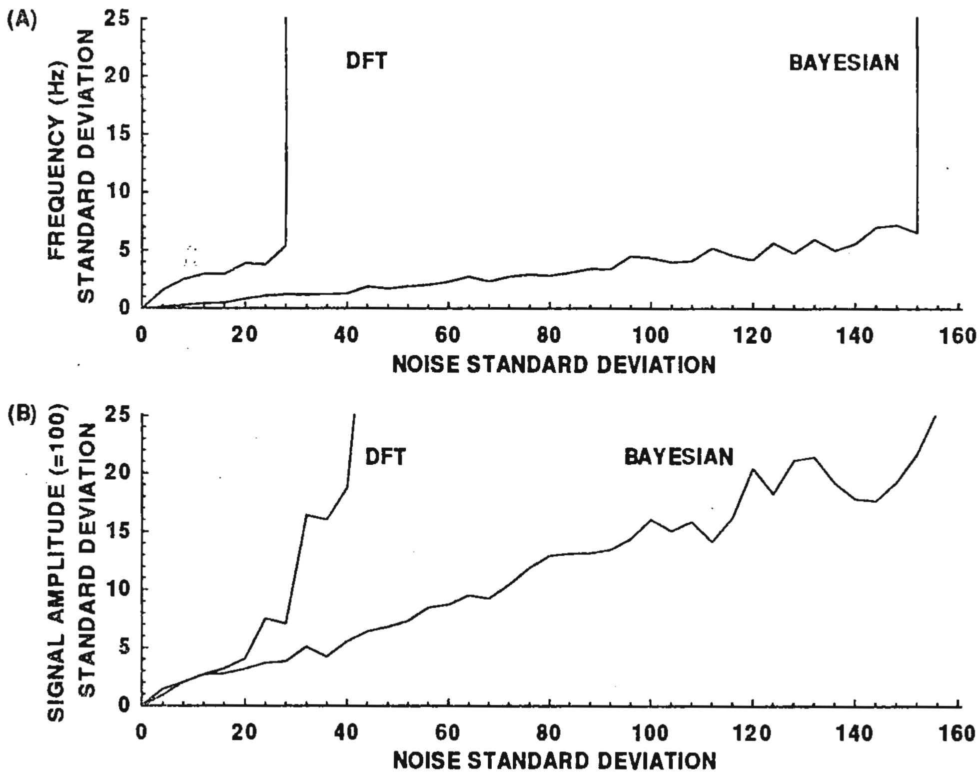

Figure. Standard deviation for (A) the frequency and (B) the signal amplitude estimates for the ^1H signal of HOD plotted as a function of the noise standard deviation. Signal parameter estimates were made repeatedly for 50 different noise "data" sets at each noise level (*i.e.*, at each noise standard deviation value) and the standard deviations for the parameter estimates were computed. The DFT estimates were obtained on an unweighted, automatically phased data set using standard Varian software, while parameters estimates for the Bayesian method were computed using procedures given in the literature (1,2).

Sincerely Yours,

John J. Kotyk   Norman G. Hoffman,   W.C. Hutton

G. Larry Bretthorst   Joseph J.H. Ackerman

1)G.L. Bretthorst, *J.Magn. Reson.*, **88**, 533-551; *ibid*, 552-570; *ibid*, 571-595.
2)G.L. Bretthorst, *J.Magn. Reson.*, submitted.

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NMR Research and Development
February 26, 1991
(received 2/28/91)

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

^{13}C-^{15}N Triple Resonance Applied to Solely ^{15}N-Labeled Peptides: Fertile or Futile?

Dear Barry,

Yes, the trumpets of triple resonance are sounding again! In our never ending quest for truth and pretty spectra, I have had the fortune of being forced to perform some initial triple resonance experiments on the solely ^{15}N-enriched linear hexapeptide FALFAL. The experiment to be described is an optimized HN(CO)(CA) in which magnetization is first transferred from ^{1}H to ^{15}N by a modified INEPT subsequence and then from $^{15}N_i$ to $^{13}CO_{i-1}$, $^{13}C_{\alpha,i-1}$, or $^{13}C_{\alpha,i}$ by the creation of heteronuclear multiple quantum coherence (HMQC), in analogy to several of the new triple resonance experiments proposed by Kay *et al.* (*1*). The ^{13}C t_1 subsequence is constructed in such a manner so that *only* the relevant ^{13}C chemical shift modulates the detected $^1H(t_3)$ signal in t_1. Magnetization is then transferred from ^{13}C back to ^{1}H in the reverse manner as previously described. The complete details and analysis of this experiment have been submitted for publication.

Figure 1 presents the 2D ^{1}H-^{13}C HN(CO)(CA) spectrum of FALFAL. The sample concentration was 3-5 mM in wet d_6-dmso. The data were collected at 27°C on a VXR500 fully equipped with three independent RF channels. The total experimental time was 8.5 hours; however, the 2D correlation peaks were visible after *only* 1-2 hours. Similar data have been collected on a UNITY-600. The sequential assignment of this linear hexapeptide is diagrammed in Fig. 1. The orientation of the sequential connectivity path was obtained from a more complete, yet more preliminary, data set in which the $H_{N,i}$-$C_{\alpha,i}$ 2D correlation peak for the N-terminus Phe residue was weakly discernible. The ^{1}H-^{13}CO correlation peaks on the left-hand side of the spectrum in Fig. 1 have been folded three times in F_1 yet can be phased to a positively absorptive lineshape because *no* linear F_1 phasing is required. It should be clear from Fig. 1 that the ability to establish the sequential connectivity path depends not on observing the ^{1}H-^{13}CO correlation peaks but rather on observing both the $^1H_{N,i}$-$^{13}C_{\alpha,i}$ and the $^1H_{N,i}$-$^{13}C_{\alpha,i-1}$ correlation peaks.

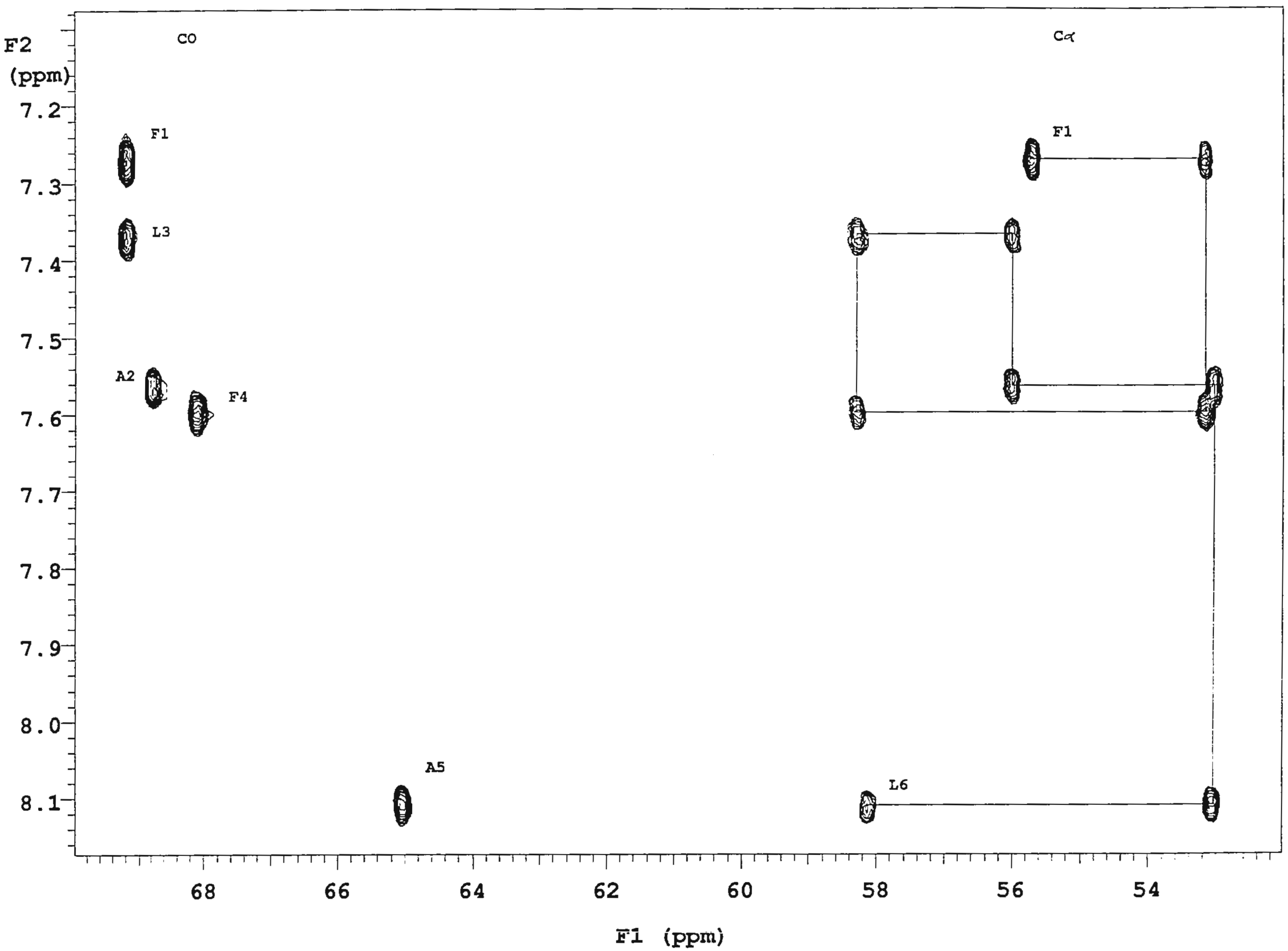
Montelione and Wagner have already pointed out that ^{13}C-^{15}N triple resonance relay experiments can be used to successfully establish the sequential connectivity of a solely ^{15}N-labeled tripeptide, albeit at a concentration of 30 mM (*2*). Fig. 1, however, points out that the general idea is applicable even at concentration levels of 3-5 mM for a hexapeptide using an optimized "out-and-back" type of triple resonance experiment. I would like to thank Ron Crouch at Borroughs Wellcome for the sample of ^{15}N-enriched FALFAL.

Sincerely yours,

Sandy Farmer

1. L.E. Kay, M. Ikura, R. Tschudin, and A. Bax, *J. Magn. Reson.* **89**, 496 (1990).

2. G.T. Montelione and G. Wagner, *J. Magn. Reson.* **87**, 183 (1990).


F2
(ppm)
CO
Cα
F1
L3
A2
F4
A5
F1
L6
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
68
66
64
62
60
58
56
54
F1 (ppm)

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February 12, 1991
(received 3/4/91)

Dr. B. Shapiro
TAMU Newsletter
966 Elsinor Court
Palo Alto, California 94303

LOW TEMPERATURE ^{31}P NMR OF Zn DIALKYLDITHIOPHOSPHATES

Dear Dr. Shapiro:

Zinc dialkyldithiophosphates (ZDTP) are important antioxidants and antiwear agents used in lubricating oils. ZDTP's are known to exist in varying proportions as either neutral ZDTP ($Zn[S_2P(OR)_2]_2$) or basic ZDTP ($OZn_4[S_2P(OR)_2]_6$)[1]. These two forms are illustrated in Figure 1 and are typically separated by a chemical shift difference of 4-5 ppm in a ^{31}P NMR spectrum (basic form is downfield of neutral form). The basic form contains six equivalent bridging $S_2P(OR)_2$ units (six equivalent P's or a single ^{31}P peak). The neutral ZDTP, on the other hand, is in a dynamic equilibrium involving a dimeric species (and possibly higher oligomeric species) and a monomeric species yielding a time-averaged spectrum of a single peak between the various neutral ZDTP's[2]. The neutral dimer ZDTP contains both bridging (P-a) and chelating (P-b1) $S_2P(OR)_2$ units (a set of two nonequivalent P's or two ^{31}P peaks) and the neutral monomeric ZDTP consists of two chelating (P-b2) $S_2P(OR)_2$ units (two equivalent P's or a single ^{31}P peak). Obviously as the ZDTP concentration is increased, the equilibrium shifts toward dimer and/or higher oligomers. Therefore the chemical shift of the neutral form is not only dependent on the OR group but also on the solvent and concentration of ZDTP in solution.

Recently we examined a neutral secondary (secondary means the OR group is derived from a secondary alcohol) ZDTP [zinc(II) bis(O,O'-diisopropyl dithiophosphate)] absent of the basic form. As expected we observed a single broad peak in the ^{31}P spectrum (Fig 2 bottom). Upon lowering the temperature from 300°K to 220°K, three peaks became evident . The low temperature ^{31}P spectrum (Fig.2, second from top) shows the two downfield peaks to be of equivalent proportions and the high field peak to be of considerably lower intensity. Upon lowering the ZDTP concentration to 1/6 that of the previous sample (Fig. 3) the intensity of the high field peak increased considerably. This indicates that the high field peak represents the P of the monomeric ZDTP and the two low field peaks are the P's of the dimeric and/or higher oligomeric ZDTP. Furthermore, since the neutral monomeric ZDTP is derived exclusively from chelating P, and the basic ZDTP exclusively from bridging P, one may assume from the chemical shifts of the dimeric ZDTP phosphorus that P-a and P-b1 represent the bridging and chelating P's of the neutral dimeric ZDTP, respectively. Finally, the low temperature (220°K) 2D exchange (NOESY) ^{31}P NMR spectrum of the neutral ZDTP (Fig. 4) illustrates the dynamic intramolecular exchange between chelating and bridging P's of the dimeric ZDTP as well as intermolecular exchange between both chelating and bridging P's of the dimeric form and chelating P's of the monomeric form.

Sincerely,

Kurt Wollenberg

Kurt Wollenberg

1) A. J. Burn, Joyner, W., Meehan, P., and Parker, K. M., *J. Chem. Soc. Chem. Commun.*, 1986, 982
2) P. G. Harrison, Kikabhai, T., *J. Chem. Soc. Dalton Trans.*, 1987, 807

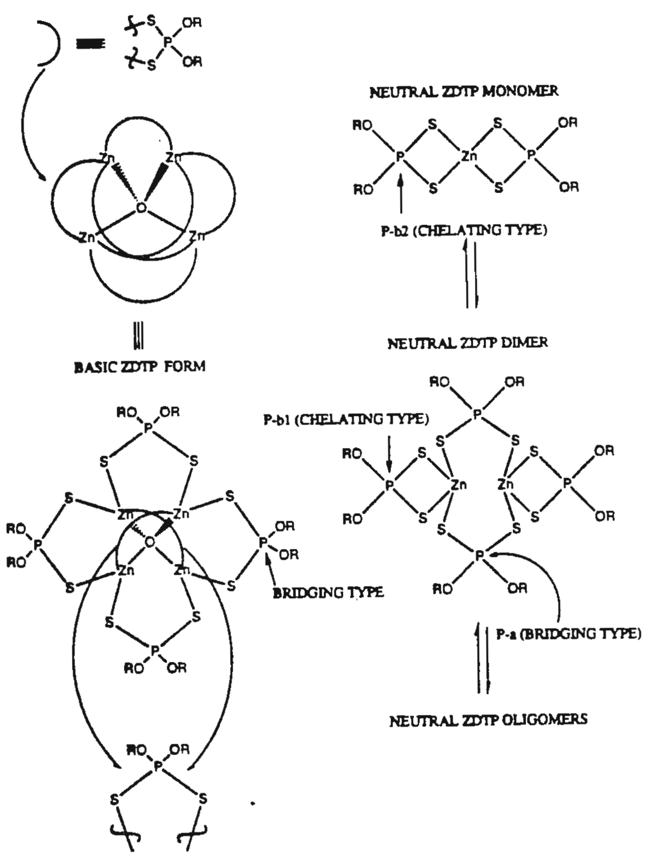

Fig. 1: Neutral (monomer, dimer), and basic representation of ZDTP

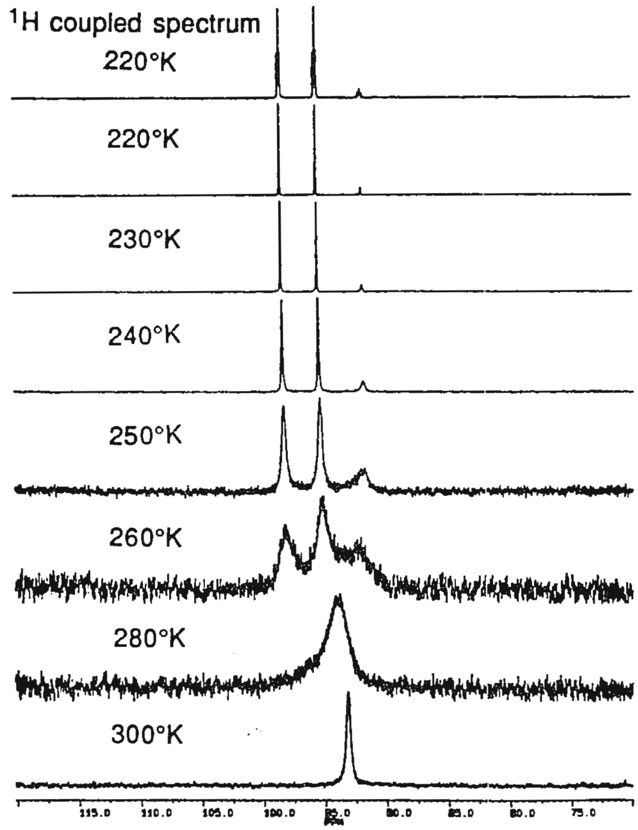

Fig. 2: 121.5 MHz ^{31}P NMR ^{1}H decoupled spectra of neutral Zinc(II) bis(O,O'-diisopropyl dithiophosphate at temperatures ranging from 300°K to 220°K (bottom to top). Top spectrum is a proton coupled spectrum and displays ^{3}J(POCH) triplet multiplicity between P and two OCH's of isopropyl. P-a, P-b1, P-b2 are defined in the text.

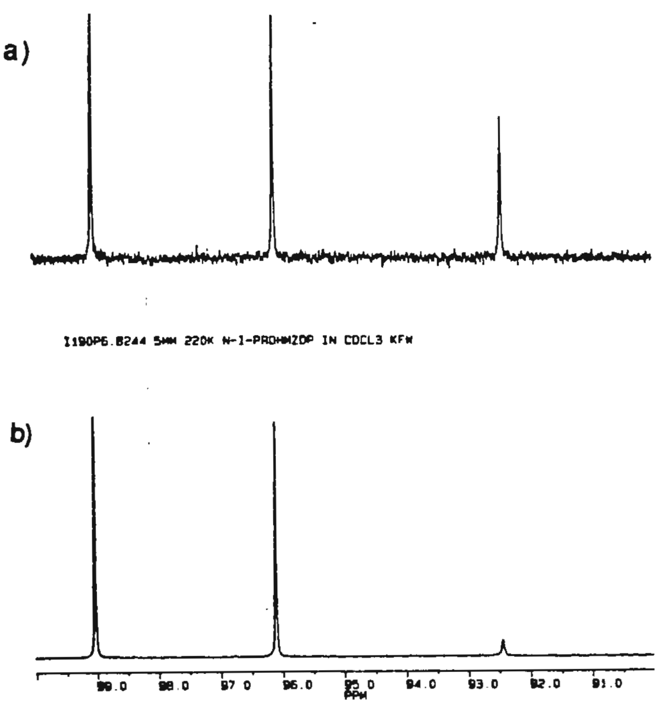

Fig. 3: 121.5 MHz ^{31}P NMR spectra of neutral Zinc(II) bis(O,O'-diisopropyl dithiophosphate (a) at 220°K and (b) at 6x the concentration of (a).

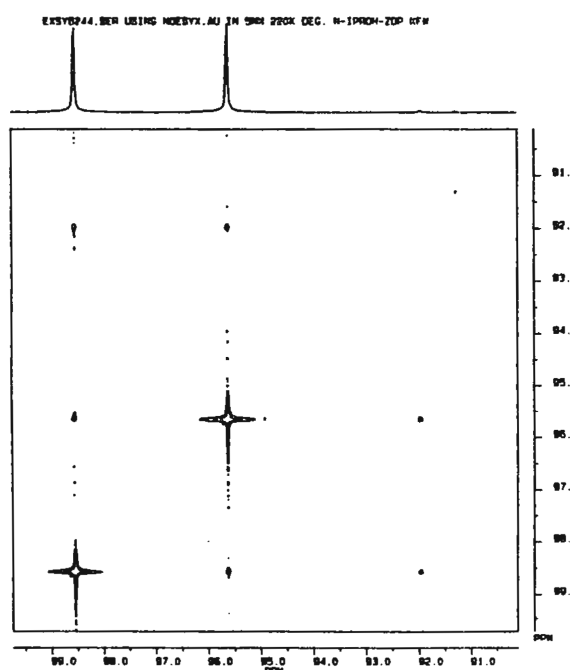

Fig.4: 2D exchange ^{31}P NMR spectrum of neutral Zinc(II) bis(O,O'-diisopropyl dithiophosphate at 220°K using a mixing time of 0.1 s.

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BRUKER/ IBM WP 200-SY Aspect 2000A, 80K memory, CDC disk drive, Oxford magnet, fully broad banded, H1 5mm and 10mm BB VSP probes.

BRUKER AC-200 Aspect 3000, 256K memory, 160 Mbyte hard drive, Oxford magnet, Cherry LCM terminal, H1 5mm BB 10mm VSP probes, fully broad banded. (new console)

BRUKER WH-270 (2Ea.) Aspect 2000A, 80K memory, CDC-32 drive, WYSE terminal, Bruker magnet, H1 5mm and C13 10mm standard probes.

BRUKER WH/WM-360 Aspect 2000A, 80 k memory, CDC-32 hard drive, H1 5mm and C13 10mm standard probes, fully broad banded, Bruker magnet.

BRUKER WM-360 Aspect 2000A, 80 K memory, 160 Mbyte hard drive, WYSE terminal, Bruker magnet, H1 5mm and C13 10mm standard probes, fully broad banded.

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NORTHWESTERN UNIVERSITY

Joseph B. Lambert
Professor of Chemistry

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Evanston, Illinois 60208-3113
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Bitnet CHEMDEPT@NUACC
Facsimile (708) 491-7713
Telex 446116 NUCHEM

March 8, 1991
(received 3/13/91)

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

Dear Barry:

We have been taking the spectra (CP/MAS) of a variety of medium rings in the solid state as a function of temperature. Many of these molecules pass through several phases. Cyclopentanol, cyclohexanol, and sulfolane, for example, go from the melt to a plastic solid, in which overall rotational motion is still fast on the NMR time scale. Over the temperature range of the plastic solid, we find that the spectrum closely resembles that of the liquid for these three molecules. The spectrum passes through coalescence close to the known plastic to nonplastic transition temperature. The spectrum then represents the collection of forms present in the nonplastic solid.

The accompanying figure illustrates the carbon-13 spectrum of cyclopentanol, which melts at -19°C. The first spectrum on the left is of the liquid at room temperature. All the rest are of the solid. Coalescence occurs at about -85°C (bottom left spectrum), and quite an array of peaks then emerges. By -140°C (bottom right spectrum), the C2 and C3 carbons are present in up to eight different environments. We are examining a variety of other plastic and nonplastic solids. This work was done by Liang Xue and Sue Howton.

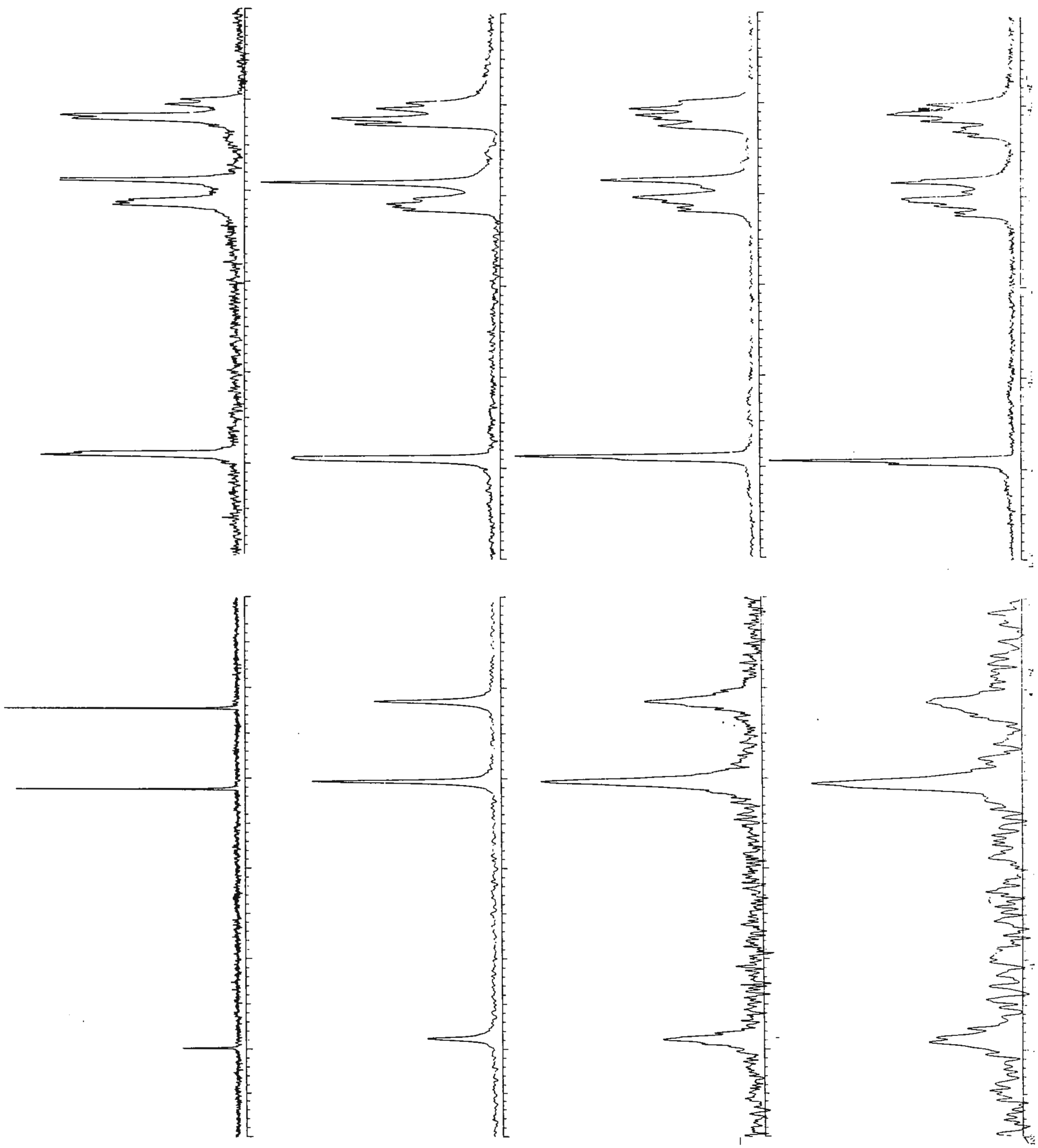
Sincerely,

Joe

Joseph B. Lambert

JBL:cs

Title: Dynamic Processes at the Plastic to Nonplastic Temperature



Northern Illinois University
DeKalb, Illinois 60115-2862

The Michael Faraday Laboratories
Department of Chemistry
(815) 753-1131

FAX (815) 753-4802

March 7, 1991 (received 3/11/91)

Professor Bernard L. Shapiro
Texas A&M University NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Re: ^{1}H and ^{13}C Assignments in Etidocaine and Etidocaine Hydrochloride

Dear Barry:

Etidocaine is one of the tertiary amine local anesthetics. It is similar to lidocaine in that it contains the same kind of aromatic ring, which is joined to the tertiary amine portion by an amide linkage, but its NMR spectrum is considerably more complicated due to the presence of an asymmetric center. In lidocaine, the NH bond is *trans* to the C=O bond in the amide group; the steric hindrance between the ortho methyl protons and the amide group causes the phenyl ring to assume a nearly perpendicular orientation with respect to the plane of the amide bond (1).

The ^{1}H and ^{13}C assignments of the free base of etidocaine in $CDCl_3$ (Figs. 1a and 1c) were easily made via a COSY and an XHCORR experiment. The ^{1}H spectrum of the hydrochloride, I, in $CDCl_3$ (Fig. 1b), shows more than simply protonation shifts. We are analyzing the complex methylene region between 3.0 and 4.0 ppm. The separation of the amide NH protons at 10.3 ppm and the methyl 11 protons into two peaks of unequal intensities (53:47), plus the further separation of these peaks upon the addition of achiral LSR indicates the presence of two stereoisomers for I. The amine NH^+ resonance appears as a broad asymmetrical peak at 10.5 ppm. The appearance of the ^{1}H spectrum is very solvent dependent. In 1:1 CD_3OD/C_5D_5N, for example, the peaks are much sharper than in $CDCl_3$, and the methine proton is a 1:1:1:1 multiplet of four lines, as expected for a group adjacent to the AB protons at 15. The ^{13}C spectrum of I in $CDCl_3$ solution is shown in Fig. 1d. Upon expansion of this spectrum, two ^{13}C peaks are observed for carbons 7 through 15. Assignments were verified via XHCORR. Achiral shift reagent ($Pr(fod)_3$) induces further shift separation of the doubled peaks.

The presence of the proton on the amine nitrogen in I is responsible for these results. In solvents such as $CDCl_3$, the nitrogen in I apparently does not invert rapidly on the NMR time scale. The C=O and NH^+ groups may be involved in an intermolecular hydrogen bond, which would further stabilize the nitrogen to inversion and may also restrict rotation about the C_9-N^+ bond, causing the line broadening. These effects create a pair of diastereoisomers of unequal population. Upon raising the temperature, the ^{13}C signals, from C_{10} and C_{12} which were separated into four peaks at 20°C, merge into two peaks at 90°C (in $CDCl_2$ $CDCl_2$ solution). At this temperature, proton exchange must be fast enough to allow a more rapid nitrogen inversion. The coalescense of the two C_{10} and two C_{12} signals is also observed for I in CD_3OD/C_5D_5N solution at 20°C. In I, the presence of a natural chiral center at C_9, in addition to the acid-induced chirality at the amine nitrogen, has resulted in a solvent-dependent diastereoisomerism.

Sincerely,

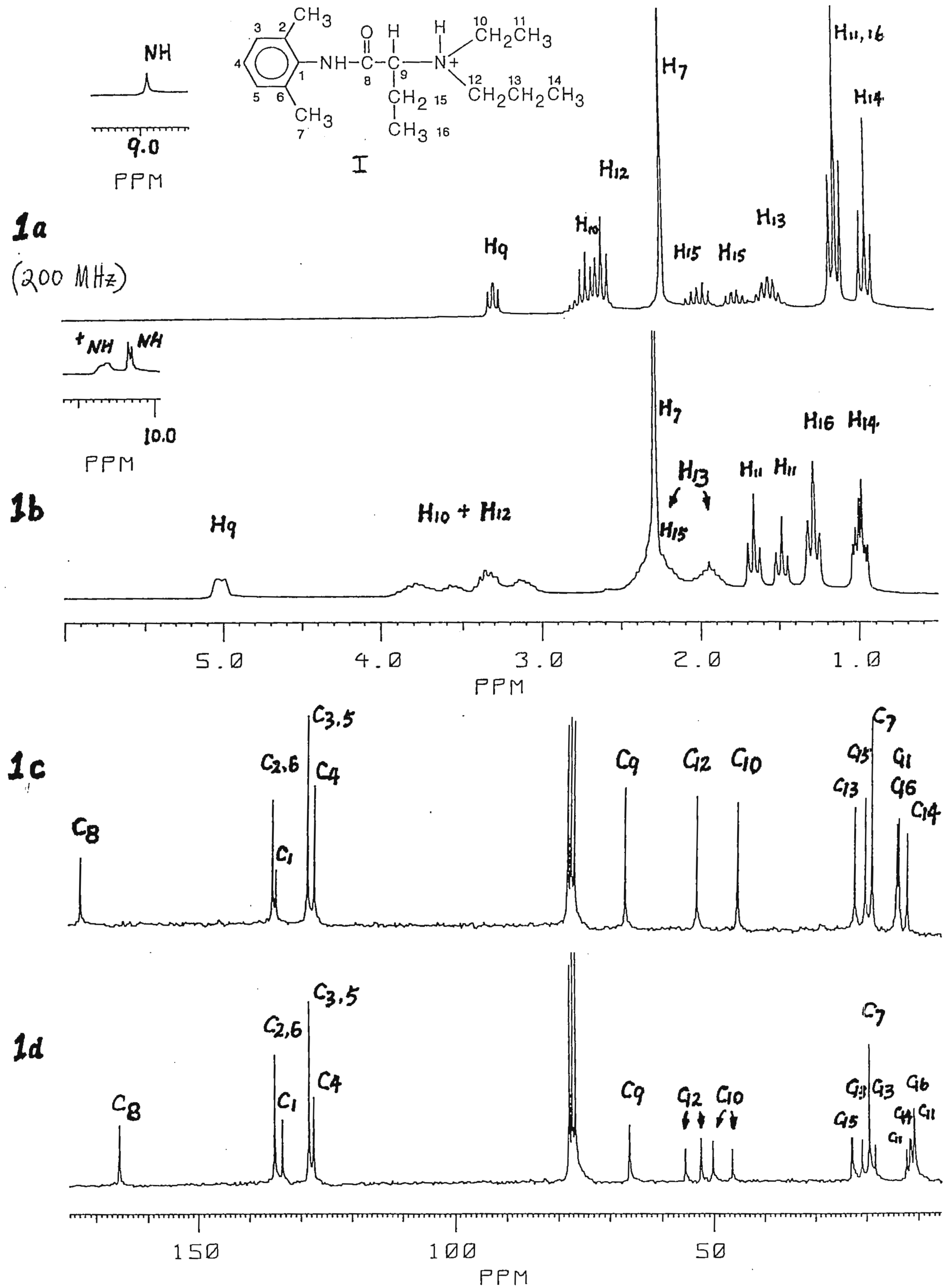
Lori

Laurine A. LaPlanche

Yangdong Xu

Yangdong Xu

1. L. A. LaPlanche, G. Vanderkooi, H. Jasmani and M. Mat Suki, Magn. Reson. Chem. 23, 945 (1985) and references therein.



NH
9.0
PPM
CH3
NH-C-C-N+
CH2CH3
CH2CH2CH3
CH2
CH3
I
1a
(200 MHz)
H7
H11,16
H14
H12
H10
H9
H15
H15
H13
+NH
NH
10.0
PPM
1b
H7
H16
H14
H13
H11
H11
H10 + H12
H9
H15
5.0
4.0
3.0
2.0
1.0
PPM
1c
C3,5
C2,6
C4
C1
C8
C9
C12
C10
C7
C15
C11
C13
C16
C14
1d
C3,5
C2,6
C4
C1
C8
C9
C12
C10
C7
C13
C13
C16
C15
C14
C11
C11
150
100
50
PPM

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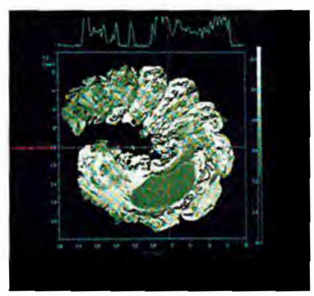

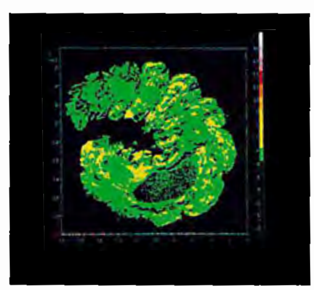

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NMR WITH A FUTURE

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DEPARTMENT OF BIOCHEMISTRY

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26 February 1991
(received 3/5/91)

Dr Bernard L. Shapiro
Editor/Publisher
TAMU Newsletter
966 Elisnore Court
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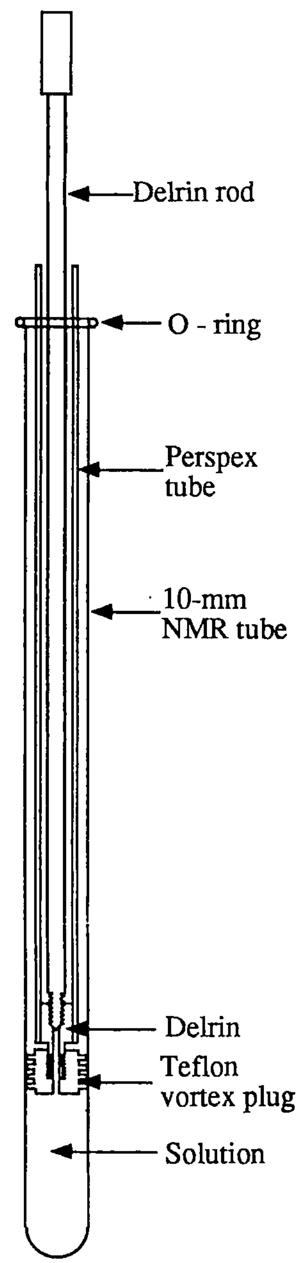
USA

Conveniently-Reversible Seal for NMR Tubes



Dear Barry,

We continue to study cell suspensions using high resolution NMR spectroscopy. We have concentrated on human erythrocytes which do not require oxygen for their metabolism but we frequently wish to study these cells with a range of different partial pressures of various gases. It is important therefore that the samples are properly sealed. For example, when we studied the exchange of $H^{13}CO_3^-$ across the human red cell membrane (a process mediated by the protein capnophorin) using T_2 relaxation analysis we initially encountered a problem with the loss of $^{13}CO_2$ from the samples. The difficulties were overcome by using a vortex plug applied right down to the meniscus of the cell suspension and then adding to the 10-mm NMR tube sufficient paraffin oil to provide an airtight seal. Sequential ^{13}C NMR spectra of the sample over several hours revealed the constancy of the $H^{13}CO_3^-$ and CO_2 resonances thus indicating a lack of evaporation of the CO_2 from the sample[1].

The use of paraffin oil is a very effective method of sealing the sample but the NMR tubes are messy to clean out and problems arise when additions need to be made to the sample. Therefore, we have devised the apparatus shown in the diagram. I hope the picture makes the design self-evident. However, it is worth noting that the whole assembly is supported on the rim of the 10-mm NMR tube by the use of a neoprene O-ring. The Teflon vortex plug is a standard commercial product but with the top screw-thread bored out to a diameter of 4.5 mm. The central rod has a thread on its lower end and a 'flat' has been filed in it to provide a passage for air to escape when the thread is slightly unscrewed. The whole device is inserted into the sample to the level of the meniscus and then the central 'tap' is screwed into place while holding the Perspex tube to prevent its rotation. When it is necessary to make additions to the sample the central Delrin rod is unsrewed a little thus allowing entry of air through the central bore as the device is pulled out. Additions can be quickly made and the sample sealed again.

The device is a rather obvious solution to the above-mentioned problem and yet it is another 'element' in the ever evolving 'folklore' of cellular NMR spectroscopy. Thanks to Dennis Leonard for useful discussions and Ross Taylor for making the device.

[1] Chapman, B.E., Kirk, K. and Kuchel, P.W. (1986) Bicarbonate Exchange Kinetics at Equilibrium Across the Erythrocyte Membrane by ^{13}C NMR. *Biochem. Biophys. Res. Commun.*, **136**, 266-272.

Yours sincerely,

Philip W. Kuchel

PHILIP W. KUCHEL
Professor of Biochemistry

Texas A&M University NMR Newsletter - Book Reviews

Book Review Editor:

William B. Smith, Texas Christian University, Fort Worth, TX 76129

" Analytical NMR "

Edited by

L. D. Field and **S. Sternhell**

John Wiley and Sons, New York, 250 pp.; 1989; $32.95; ISBN 0 471 91714 1

This book is aimed at those practicing chemists and students who wish to know how NMR may help them in the solution of their analytical problems. After a brief introductory chapter by the authors, the balance of the text consists of contributions as follows: Chap. 2, Fundamental Aspects of NMR Spectroscopy (L.D. Field); Chap. 3, Quantitative Applications of ^{13}C NMR (J.R. Mooney); Chap. 4, Analysis of Fossil Fuels (C.E. Snape); Chap. 5, NMR of Zeolites, Silicates and Solid Catalysts (A.D.H. Clague and N.C. M. Alma); Chap. 6, Biological Applications of NMR (P.W. Kuchel); and Chap. 7, Automatic NMR Analysis (M. Sproul and R.-D. Reinhardt).

Chapter 2 is meant to tie together the various techniques discussed in subsequent chapters so that the initiate to NMR will not be cast adrift with only his sophomore organic textbook as background in the subject. This is not a book that will have wide applicability to those who are already deeply enmeshed in the topic of analytical NMR. Chapter 3 reviews and updates the original work published in 1974 by Jim Shoolery, and extends into measurements on solid systems. Chapters 4 and 5 continue with solids NMR considerations in the systems named. Entire books have, of course, been written on the topics covered in Chapter 6.

Useful references to the more detailed literature are given throughout. Organic chemists were attracted to Bloch's early lectures on NMR by the fact that one could plainly see that the various protons in ethanol came in the ratio 3:2:1. Instruments such as the Varian A-60 an HA-100 gave more accurate proton integrations than today's high field pulse instruments unless very special care is taken. It is perhaps strange that this topic is no longer considered worthy of mention.

W.B.S.

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

UNOCAL 76

February 10, 1991
(received 2/22/91)

Prof. B. L. Shapiro
968 Elsinore Court
Palo Alto, CA 94303

Wideline ^{51}V NMR Of Cracking Catalysts

Dear Prof. Shapiro,

Both nickel and vanadium contamination are known to catalyze undesirable side reactions during petroleum refining processes. Understanding the role of vanadium in the deactivation of FCC (Fluid Cracking Catalysts) is therefore a topic of interest to petrochemical research. As a prelude to studying the FCC system(typically a combination of gel, clay and zeolite) itself, we initiated a solid-state (wideline and MAS) ^{51}V NMR investigation of aluminas and aluminosilicate gels that were systematically impregnated with varying concentrations of vanadium . Preliminary results from wideline NMR spectra have proved to be particularly useful for differentiating between various vanadium (V^{+5}) surface species present.

Room temperature measurements were carried out using a General Electric GN-300 spectrometer, equipped with an Explorer high speed digitizer and a 7 mm multi-nuclear MAS-NMR probe from Doty Scientific. Spectra were typically obtained using a simple one-pulse sequence (Bloch decay). Besides avoiding complications that arise from varying degrees of excitation selectivity that become important with the longer pulse lengths needed to generate 90^{o} and 180^{o} pulses for a spin-echo measurement, we find the use of Bloch decays render more resolved albeit "distorted" spectra with more accentuated valleys between peaks and shoulders. The 79 MHZ wideline ^{51}V NMR spectra of a series of steam aged pseudo-bohemite samples containing 0.5 to 5.0% V (loaded using VO^{+2}-naphthenate) are shown in *Figure 1*. While low surface coverages favor the formation of a highly disordered four-coordinated vanadium species, an increasing amount of vanadium is present in a six-coordinate environment at higher surface coverages . This environment is identified by a highly distorted lineshape revealing a close to an axial CSA tensor ($\sigma_{\perp}$ ~ -300 ppm). Upon dehydration, this site disappears and spectra characteristic of a 4-coordinate vanadium species emerge (see *Figure 2)* showing that hydrous species (H_2O and/or OH) participate in the six-coordinate environment.

The major focus in this study was site differentiating via chemical shift dominated NMR lineshapes. In addition, quadrupolar interaction manifests itself in varying degrees of excitation selectivity for the central +1/2 to -1/2 transition. *Figure 3* shows examples of vanadium on aluminosilicate gel, where this was exploited for spectral edition purposes. It illustrates how it is possible to selectively detect signals of interest by using pulses of sufficient length to cause relaxation of the other NMR signals in the rotating frame of the applied radio frequency field. Thus, at a pulse length of 7 µs, the sharp 500 ppm feature, which arises from ^{51}V nuclei with significantly stronger quadrupolar interactions, remain undetected in this aluminosilicate gel sample loaded with 3% V. Based on other evidences including its wideline NMR profile, the observed spinning side patterns observed under MAS conditions, Raman and XRD data, we assign the signal observed using a 7 µs pulse to the presence of amorphous V_2O_5. A detailed account of this study is due appear in print shortly.

Please credit this contribution to Pradeep Iyer's account.

Sincerely Yours,

Mario L. Occelli

Hellmut Eckert
Dept. of Chemistry
UC, Santa Barbara

Pradeep Iyer

79 MHZ ^{51}V Wideline NMR Spectra

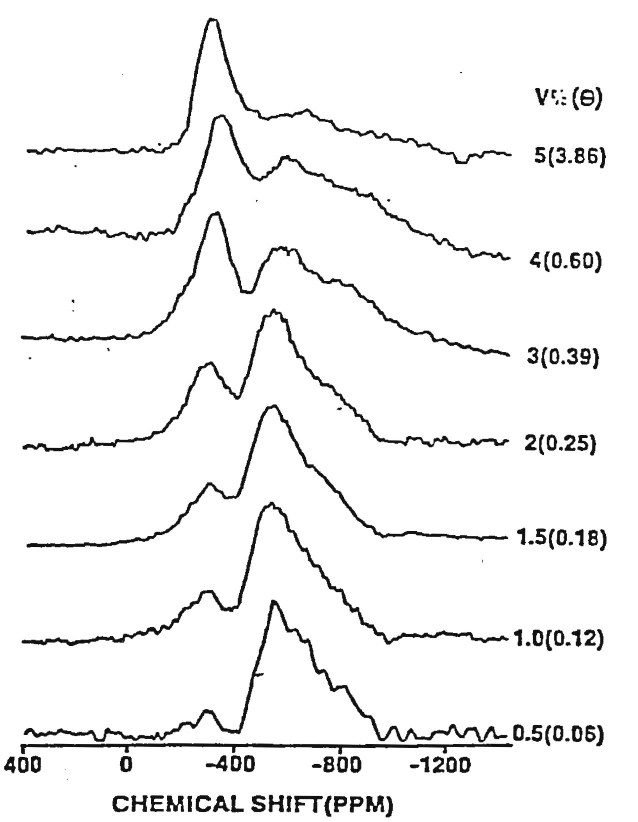


Figure 1. V-loaded aluminas (boehmite loaded with VO^{+2} naphthenate in benzene and steam aged). The numerals indicate V loading and (θ)surface coverage.

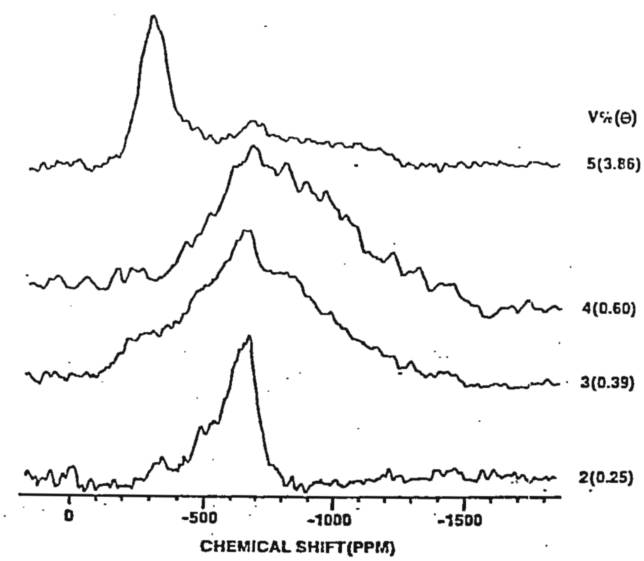


Figure 2. V-loaded aluminas after dehydration in vacuo at 220 °C.

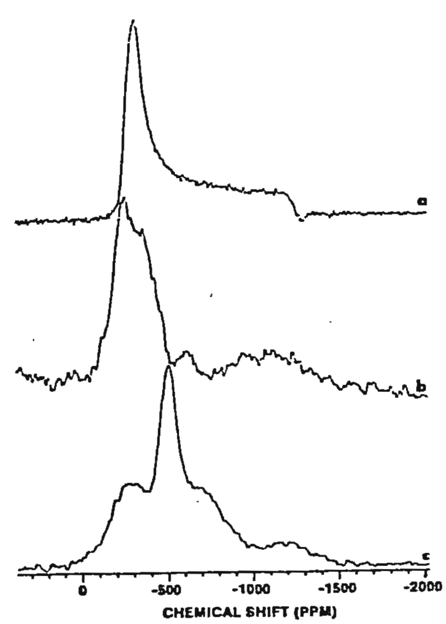


Figure 3. Effects of pulse length on ^{51}V NMR spectra of aluminosilicate gels containing: (a) 5% V, 7 µs pulse length resulting in exclusive detection of crystalline V_2O_5; (b) 3% V, 7 µs pulse length resulting in exclusive detection of amorphous V_2O_5; and (c) 3% V, 1 µs pulse length, rendering a spectrum representative of all V^{+5} species present.

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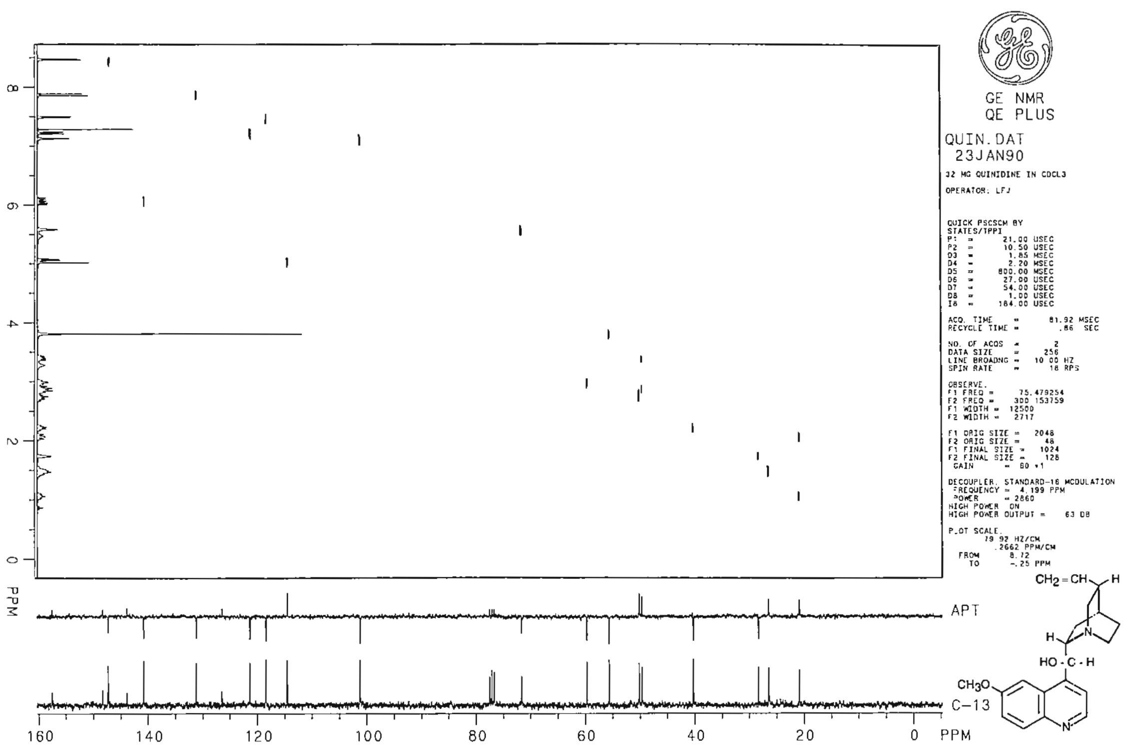

An automated run using MACRO mode operation on a sample of 32 mg of quinidine in 0.5 ml chloroform-d (0.20M). Data were obtained using the 5 mm broadband probe. ^{1}H, ^{13}C, APT and phase sensitive 2D data were collected, processed and plotted—including the 2D contour—in only 8.2 min.

Duke University

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LEONARD D. SPICER, DIRECTOR
ANTHONY A. RIBEIRO, MANAGER

(919) 684-4327
(919) 684-6287

February 12, 1991
(received 2/19/91)

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

Continuing Long Range (LR) Walking

Dear Barry,

I describe some aspects of two LR HC walks on clinically important benzofuran-type heart drugs. The molecules (see structure on next page) feature several quaternary carbons and oxygen, nitrogen and iodine heteroatoms.

The first is a 2D LR experiment with BIRD operator (1). The hard 1H decoupler pulse here calibrated at 12 usec. Fig 1 shows results for the derivative where R=CH2 at C3 of benzofuran and R′=ethyl group. The 2D plot is just above noise. The correlation from the 3-CH2 protons shows five strong and 2 weak responses. The 27 ppm response is a weak direct response from incomplete suppression of one-bond modulation, while the 91 ppm response is a weak four-bond correlation to the iodinated carbons. The 5 strong responses are 2- and 3-bond correlations to quaternary and CH carbons in the benzofuran and iodinated phenyl rings.

The second is the 1D selective INEPT experiment with soft decoupler pulses (2). The soft decoupler pulse calibrated at 10 msec (~25 Hz rf field). Pulsing the 3-CH2 protons (Fig. 2) excites the same five strong correlations seen in the 2D experiment. When the CH2N protons at 3.7 ppm are excited, LR responses are seen at the OCH2 and ethyl CH2 carbons. These LR responses were not detected in the 2D experiment. The ethyl CH2 carbon response is especially satisfying since this indicates successful transfer of magnetization across the nitrogen heteroatom to the two ethyl groups. Selective INEPT is however not without its own perils, as pulsing the 3.4 ppm ethyl CH2 elicited an "extra" response from the 3-CH2 carbons at 27 ppm, indicating a coincidental excitation of the 3-CH2 13C satellite (2). A detailed report on these long range molecular walking experiences is in press (3).

The experiments were carried out on our GE GN-300 wide-bore spectrometer with 5mm H/C probe. I thank Roy Johnson of GE NMR for helpful discussions.

Sincerely,

Tony

Anthony A. Ribeiro

1. A. Zekster et al, Mag. Res. Chem. 25 752 (1987).
2. A. Bax, J. Mag. Res. 57 314 (1984).
3. A.A. Ribeiro & G.L. Jendrasiak, Mag. Res. Chem.,in press.

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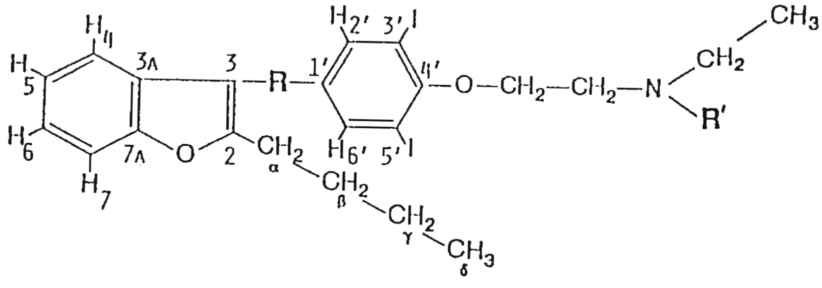
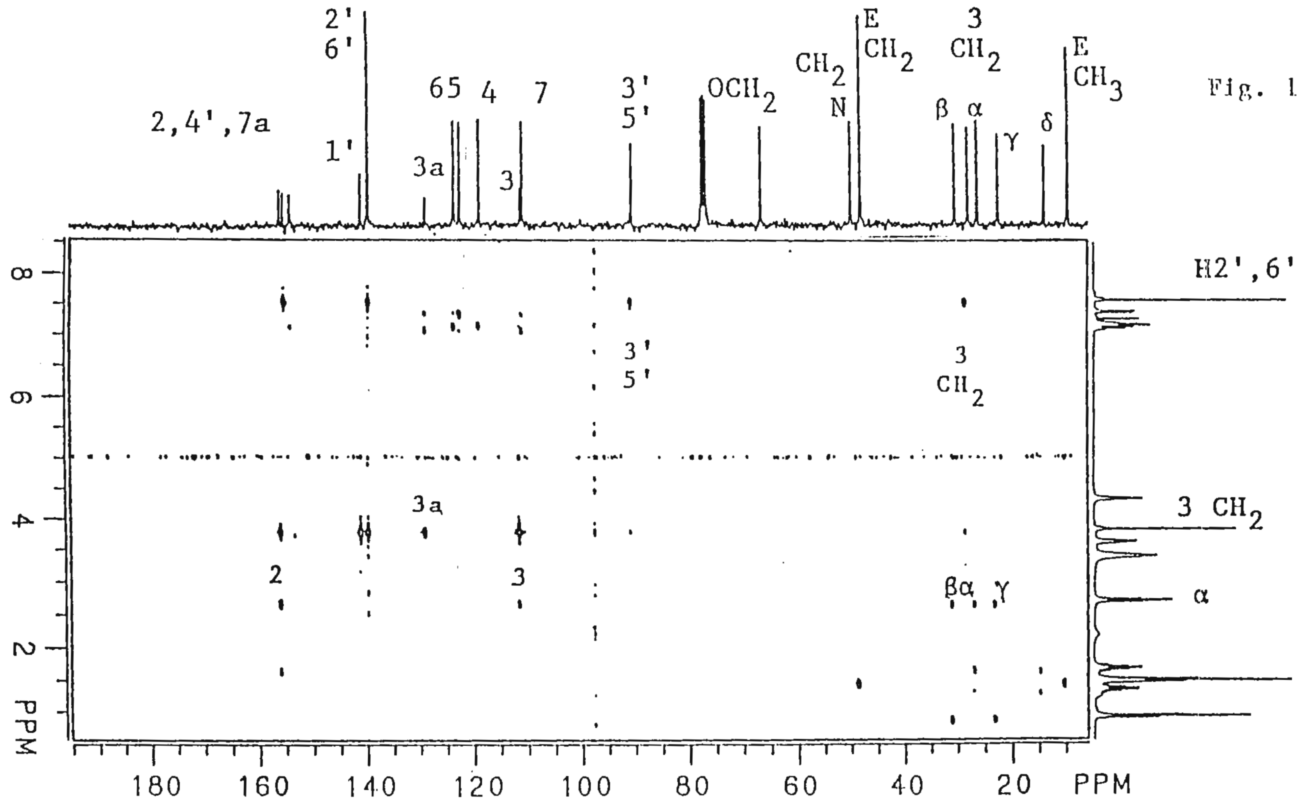

3A
3
R
1'
4'
O—CH2—CH2—N
CH2
CH3
R'
7A
O
2
CH2
CH2
CH2
CH3
I
I


2,4',7a
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β
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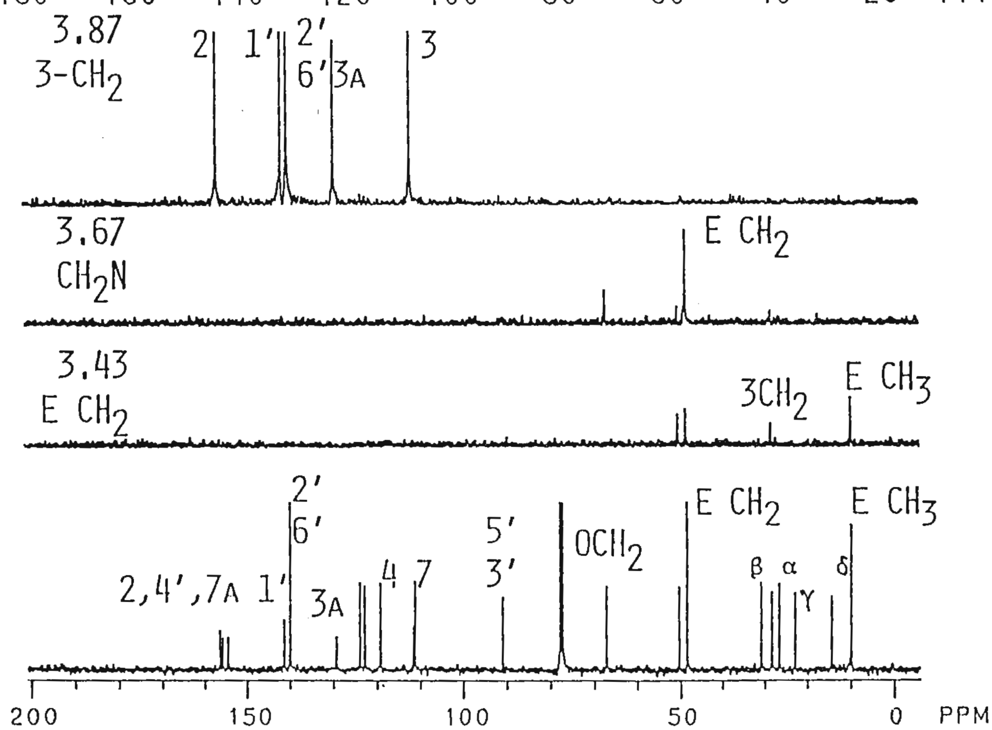
Fig. 1


3.87
3-CH2
2
1'
2'
6'
3A
3
3.67
CH2N
E CH2
3.43
E CH2
3CH2
E CH3
2,4',7A
1'
2'
6'
3A
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7
5'
3'
OCH2
E CH2
β
α
γ
δ
E CH3
200
150
100
50
0
PPM

Fig. 2

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MIAMI VALLEY LABORATORIES
P. O. BOX 398707, CINCINNATI, OHIO 45239-8707

February 28, 1991
(received 3/4/91)

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

The Procter and Gamble Company's New MRI/S Facility:
ECG-Gated Imaging with the Biospec and the Physiogard Monitor

Dr. Shapiro:

This letter will serve as an introduction to the new Magnetic Resonance Imaging/Spectroscopy (MRI/S) Facility located at Procter and Gamble's Miami Valley Laboratories. We have a Bruker Biospec imaging spectrometer with a 4.7 T magnet housed in an RF-shielded room, which allows free access to the 30 cm bore. Two sets of gradient coils and a pair of volume coils allow imaging of objects which will fit into a "sweet spot" which is defined by a sphere of approximately 9 cm diameter. Gradient preemphasis is completely computer-controlled. The Biospec does not have a windows-like software environment; rather it has two monitors, one for graphics display and one for computer communication. The system is controlled by the venerable Aspect 3000 computer, which is connected by fiber optic cable to Bruker's UNIX-based X32 workstation. At present the X32 is largely used for data archival but we hope to use existing software to perform 3D reconstruction of image data. The WORM optical drive is an essential component as each image typically occupies 0.25 Mbyte of disk space. Best of all, the Biospec's gradient amplifiers, RF transmitters, power conditioners, computer, and disk drive occupy a room separated from the console area; this suppresses fan noise and creates a very quiet working environment. In addition to the Biospec and the X32 areas, the MRI/S Facility contains a large laboratory for sample preparation, a workbench for RF coil construction, and office space for two staff (Tom Neubecker and me) and a technician or two.

Now for the technical portion of this letter. ECG-gated imaging with the Biospec is controlled by the SM785 Physiogard monitor, which is normally used for human studies. Thus some modifications must be in place to allow proper operation with animals with rapid heart rates. ECG leads can be made from a length of shielded 4-wire cable attached to a 5-pin DIN connector. Pins 3 and 4 should be jumpered together inside the connector. Pins 1 and 2 connect to wires which will be placed near the heart and pin 5 is connected to the reference wire. To place the leads on small animals, I use a suggestion from Debbie Burstein of Beth Israel Hospital: after anesthetizing an animal, I insert a 16-gauge needle through a fold in the skin, place the lead in the needle bore, and remove the needle, leaving the lead imbedded. Because small animal heart cycles are short, the Physiogard's normal pattern-matching 'Software' mode cannot be used, and the unit must be placed in 'Hardware' mode by depressing the 'QRS' button after turning the monitor on. Most of these tidbits are not available in the out-dated German manual we received; however, I have been informed that a revised manual in English is being written. Finally, the standard Bruker imaging sequences perform multislice excitation after triggering from a single point in the QRS complex; this means that each slice is excited at a different point in the heart cycle. I, like others, have modified the Bruker software such that each slice is gated to the same point in the heart cycle and a menu-controlled delay is placed between the trigger pulse and slice excitation. The modifications can be made available on request.

Our work now is largely exploratory and pedagogic. The MRI/S Facility has generated a lot of excitement as shown by the attendance at our "Opening Event" last October. Thus we are faced with the need to teach potential in-house collaborators the capabilities of the technology and attempt to make measurements which will support the development of new products. We already have customers willing to test our abilities and anticipate an exciting year.

Sincerely,

THE PROCTER & GAMBLE COMPANY
Research & Development Department

Michael D. Cockman

Michael D. Cockman, Ph.D.
Health & Personal Care Tech. Div.

Please credit this letter to the account of Bob Honkonen.

TELEPHONE
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TELEGRAMS
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POSTERA CRESCAM LAUDE

The University of Melbourne

SCHOOL OF CHEMISTRY
Fax + 61 3 347 5180

Parkville, Victoria 3052

4 March 1991
(received 3/8/91)

Dr Barry L. Shapiro
Editor, TAMU Newsletter
966 Elsimore Crt
PALO ALTO CA 94303
U.S.A.

Dear Barry,

AUSTRALIAN NMR CONFERENCE

The Eighth Australian NMR conference will be held in Lorne, Victoria, 2-6 February 1992. There will be invited lectures in theory and applications of NMR plus contributed papers and posters. We hope that you and your colleagues may be able to participate in this conference. Lorne is a seaside resort approximately 80 miles south-west of Melbourne. Those who attended in 1983 will remember Lorne for the bushfire that swept through the area as well as for the science. We are hoping for a minimum of the former and a maximum of the latter! Additional information will be forthcoming. Please advise us of your interest by writing to:

Professor D.J. Craik, Victorian College of Pharmacy, 381 Royal Parade,
PARKVILLE, Victoria 3052, Australia.
Phone: 387 7222. Fax: 389 9582

Yours sincerely,

David

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Bruker gives you exceptional freedom in the choice of industry-standard computers by delivering NMR software for multi-vendor networks. The UNIX*-based software (UXNMR) is available for SGI IRIS* workstations, IBM RS/6000* systems, and SUN* SPARCstations.* The new graphics use X-Windows* and the Motif interface toolkit. Via Ethernet* (TCP/IP), it can be run remotely from any X-server.

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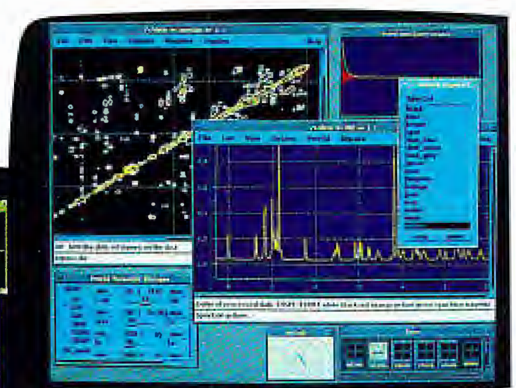

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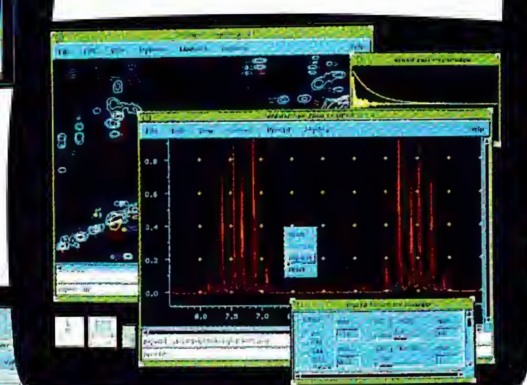
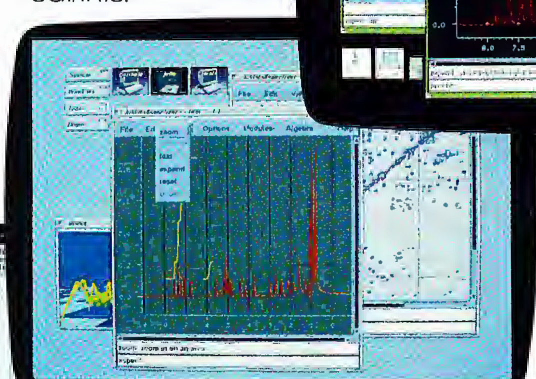
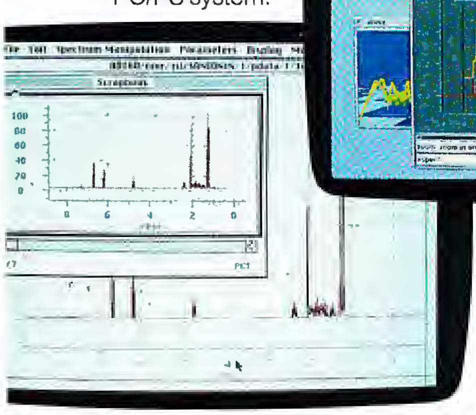


UXNMR on your SGI/IRIS.



UXNMR on your SUN SPARCstation.



WINNMR on your Mac II or PC/PS system.

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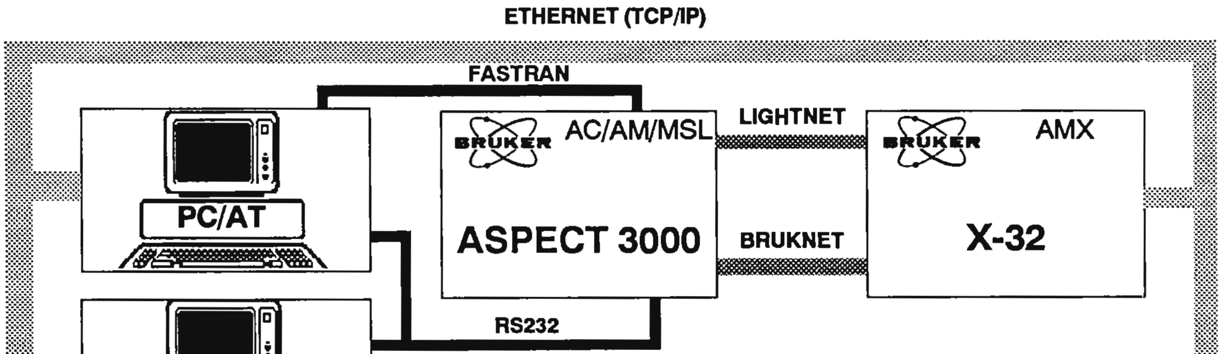

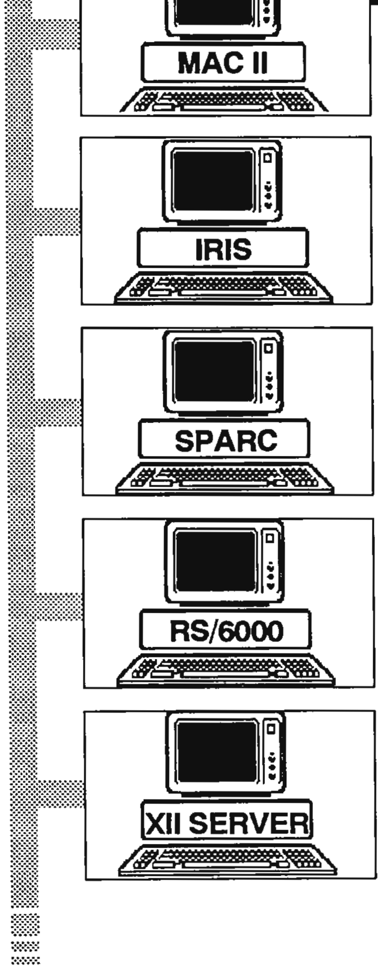

Bruker now offers a software package, UXNMR/P, that runs on industry standard computers. UXNMR/P is a ported version of the UNIX-based NMR processing software, UXNMR, that runs on the AMX console and X-32 computer. The ported package is designed for use in a networked laboratory environment with computers from different vendors. We show UXNMR/P running on the SUN SPARC, SGI IRIS, and the IBM RS/6000.

The graphics for UXNMR/P make use of the X11 Window System for convenient access of networked computers. A terminal working as an X11 server can execute UXNMR/P running on any CPU available on the network. The user interaction and the graphics output are processed by the X11 server itself, running on the users desktop.

Bruker also offers a NMR software processing package (WIN-NMR) to run under MS-WINDOWS on IBM/AT compatible PCs. A version is also available to run on Macintosh II computers.

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10/90

UNIVERSITY OF UMEÅ
Department of Physical Chemistry

^{2}H-NMR on Bilayers of *Acholeplasma* Glucolipids.

Dear Prof Shapiro, Umeå February 26, 1991 (received 3/4/91)

We have recently used our Bruker AM 500 spectrometer for ^{2}H-NMR studies of lipid bilayers of glucolipids from *Acholeplasma laidlawii*.[1] Perdeuterated palmitic acid was biosynthetically incorporated into the membrane lipids and the two dominating glucolipids, monoglucosyldiglyceride (MGlcDG) and diglucosyldiglyceride (DGlcDG), were isolated and purified. A series of samples containing mixtures of labelled and unlabelled glucolipids were prepared. The order parameter profile and the dynamics of the acyl chain were studied by ^{2}H-NMR. It was found that the order of acyl chain depends on the headgroup composition in the lipid bilayer; a large headgroup (DGlcDG) gives a lower acyl chain order and addition of a lipid with a smaller headgroup (MGlcDG) increases the order of DGlcDG. The relaxation data indicated that the bilayer curvature increases with an increased amount of the glucolipid which has a tendency to form non-bilayer structures (MGlcDG) i.e. with the closeness to a non-bilayer phase.

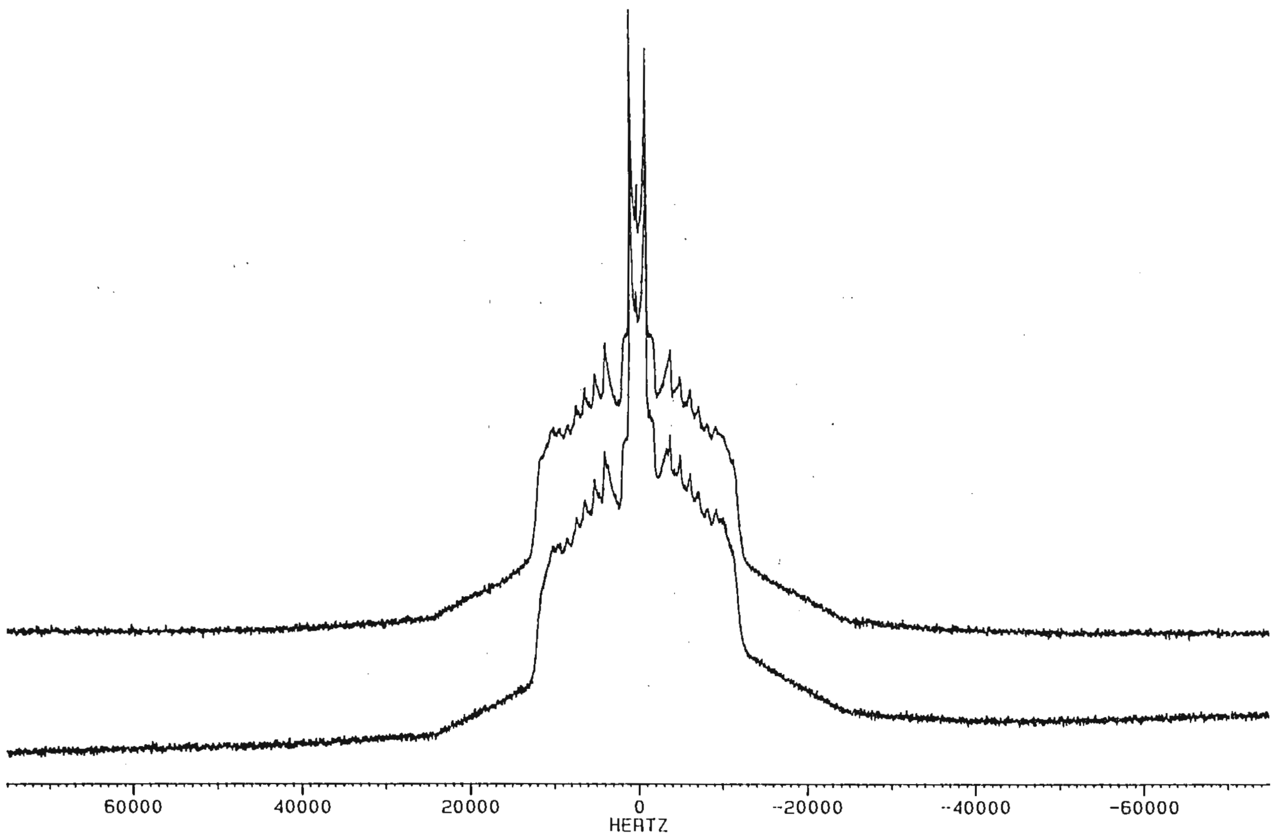
Even though the AM 500 spectrometer is a high resolution "low power" instrument, we found that studies of the liquid crystalline phases could be done without any extra high power transmitter equipment. With the standard Bruker transmitter, of type BS-V 8, we got a 90 degree pulse length of 14 μs on a Bruker 10 mm broadband high resolution probe and 5.5 μs on a Cryomagnetics-made probe with an 8 mm horizontal solenoid. A 90 degree pulse of 14.2 μs covers the spectral region of the liquid crystalline phases fairly well; e.g. the attenuation factor[2] at an offset of 25 kHz is 0.457. Even the presence of a gel phase, with a maximum splitting of 125 kHz, could be detected with 45 degree pulses of 7.2 μs.

The spectra were all acquired with the quadrupole echo technique,[3] which effectively eliminates baseline problems due to filter effects and pulse breakthrough. As was discussed by Marion and Bax,[4] when the signal is sampled alternately in the real and imaginary channels ("sequential acquisition") the baseline is tilted if the signals in the two quadrature channels are of mixed phase. Using the digital phase shifter of the AM-spectrometer for the pulses, we could acquire spectra in pure phase. (On an MSL-instrument the phase adjustment is more easily done directly on the receiver using the RCPH command.) Typical spectra are shown in the Figure overleaf. As a result of acquiring the spectrum in pure phase the baseline tilt is absent in the upper spectrum.[5]

With the best regards,

Per-Olof Eriksson
Department of Physical Chemistry
University of Umeå, S-901 87 Umeå, Sweden.

1. Eriksson, P.O.; Rilfors, L.; Wieslander, Å.; Lundberg, A.; Lindblom, G. *Biochemistry*, in press
2. Bloom, M.; Davis, J. H.; Valic, M. I. (1980) *Can. J. Phys. 58*, 1510.
3. Davis, J. H.; Jeffrey, K. R.; Bloom, M.; Valic, M. I.; Higgs, T. P. (1976) *Chem. Phys. Lett. 42*, 390.
4. Marion, D.; Bax., A. (1988) *J. Magn. Res. 79*, 352
5. Please credit this contribution to the account of Ulf Edlund, University of Umeå.



^{2}*H-NMR quadrupole echo spectra of bilayers of diglucosyldiacylglyceride containing perdeuterated palmitic acid at 27 °C. The spectra were acquired on a Bruker AM500 spectrometer with a broadband high resolution probe with 90 degree pulses of 14 μs. The pulses were digitally phase shifted so that the real quadrature channel contained pure absorptive signal only (upper spectrum), and an equal mixture of absorptive and dispersive signal (lower spectrum).*

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

March 11, 1991
(received 3/13/91)

Dear Barry, E-Mail for Bruker Users. PTS Clock Problem. Surplus EM-390 Parts.

E-MAIL:

Having used E-mail to correspond with some users of Bruker spectrometers, I thought that some of the exchange could be of general interest. Late last year I decided to try starting an electronic mailing list for users of Bruker nmr spectrometers. The purpose is to foster an exchange of questions and ideas, pulse programs, software and utilities, fixes for hardware problems etc. via the speed and convenience of electronic mail.

Frequently, a particular problem one is trying to solve may well have been successfully tackled elsewhere. An inquiry to the subscribers of the list may quickly provide answer. On at least one occasion, we would have spent hours getting an experiment to work had not one of the subscribers pointed out a subtle problem.

Currently we are using an account on one of the campus computers. At this point, I manually forward incoming mail to subscribers. We expect to get our own UNIX workstation shortly; then we will be able to automate distribution.

We have access to a campus computer for file transfers via FTP. This can be used for up- and down-loading of source code as well as executable programs without having to mail tapes or floppy disks.

Anyone wishing to participate should send E-mail to *nunlist@garnet.berkeley.edu.*

PTS Clock Problem:

A few days ago we noticed that the lock level on our 1984 AM-500 would suddenly decrease by about 30 % and quickly recover. This happened every few seconds. The appearance of single scan proton spectra suggested a severe field and/or frequency stability problem. Substituting the 10 MHz clock from another synthesizer eliminated the instability. Comparing the suspect clock against the variable frequency output of the other synthesizer (adjusted to match the difference of the exact clock frequencies) with a scope in X-Y mode revealed sudden jumps of phase or frequency. We have no idea if this failure of the otherwise extremely reliable synthesizer occurred all of a sudden or more gradually. A gradual deterioration could possibly cause a substantial increase in 2D t_1-noise before anything seems amiss in 1D spectra.

Surplus EM-390 Parts:

We have an EM-390 spin decoupler and V.T. control unit (electronics unit only) which are no longer used. Both were working when they were last used. If anyone has any use for either, please contact me.

Best Regards, Rudi Nunlist

Rudi

391-44

Washington
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Department of Chemistry

Final Announcement

Fifth Washington University-ENI/Emerson Electric Company Symposium on Nuclear Magnetic Resonance

Monday, May 20, 1991

A symposium on modern techniques in nuclear magnetic resonance will be held from 8:45 a.m. to 5:00 p.m., Monday, May 20, 1991 in Louderman Hall, Room 458, Department of Chemistry, Washington University, St. Louis, Missouri.

Lecture Schedule

* **Ray Freeman** - University of Cambridge
  New Approaches to the Design of NMR Experiments

(Refreshment break)

* **Chien Ho** - Carnegie Mellon University
  Recent NMR and Molecular Biological Studies of Structural Properties and Interactions of Membrane-Associated Proteins

* **Robert S. Balaban** - National Institutes of Health
  Macromolecule-Water Magnetization Transfer: A Molecular Basis for Magnetic Resonance Image Contrast

(Lunch)

* **Thomas L. James** - University of California, San Francisco
  Refinement of DNA and Protein Structures in Solution Using NMR Data

(Refreshment break)

* **Hans W. Speiss** - Max-Planck-Institut für Polymerforschung
  Two- and Three-Dimensional Solid State NMR and Application to Synthetic Polymers

(Social Hour and Reception)* - *Women's Building, adjacent to Louderman Hall

The symposium, sponsored by Emerson Electric Company, is open to all interested in the development and application of new techniques in nuclear magnetic resonance. Those planning to attend are requested to fill out and return the enclosed self-addressed reply card. All attendees are invited to Lunch and to the Social Hour and Reception. For additional information, contact departmental secretary, Mary Ann Wiegers, at (314) 889-6530.

Symposium visitors are asked to park in the lots indicated on the map (reverse side of this announcement). It will not be necessary for you to park in the metered visitor parking areas.

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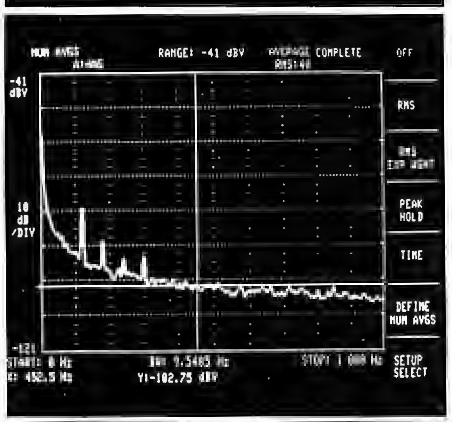

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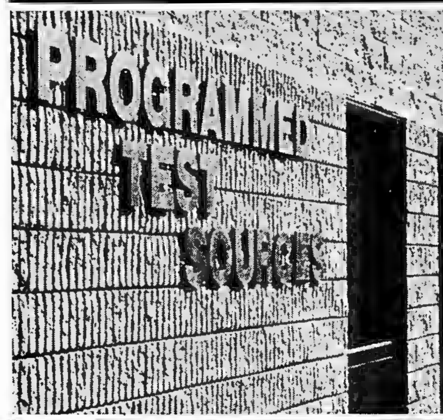

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Range: 90-120 MHz
Resolution: 0.1Hz-100KHz (opt)
Switching: 1-20μs

Output: +3 to +10dBm; 50ohm
Spurious Outputs: −75dBc
Phase Noise: −75dBc (0.5Hz-15KHz)

Freq. St'd: OCXO, TCXO, Ext.
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Range: 0.1-160 MHz
Resolution: 0.1Hz-100KHz (opt)
Switching: 1-20μs

Output: +3 to +13dBm; 50ohm
Spurious Outputs: −75dBc
Phase Noise: −63dBc (0.5Hz-15KHz)

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Range: 1-250 MHz
Resolution: 0.1Hz-100KHz (opt)
Switching: 1-20μs

Output: +3 to +13dBm; 50ohm
Spurious Outputs: −70dBc
Phase Noise: −63dBc (0.5Hz-15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: $7,155.00*

PTS 300

Range: 0.1-300 MHz
Resolution: 1Hz
Switching: 1-20μs
Phase Continuous: 1Hz-100KHz steps

Output: +3 to +13dBm; 50ohm
Spurious Outputs: Type 1 −70/65 (typ/spec); Type 2 −65/60dBc
Phase Noise: −68dBc (0.5Hz-15KHz); −63dBc

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: Type 1 $6,175.00*; Type 2 $5,625.00*

PTS 500

Range: 1-500 MHz
Resolution: 0.1Hz-100KHz (opt)
Switching: 1-20μs

Output: +3 to +13dBm; 50ohm
Spurious Outputs: −70dBc
Phase Noise: −63dBc (0.5Hz-15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: $8,385.00*

PTS 620

Range: 1-620 MHz
Resolution: 0.1Hz-100KHz (opt)
Switching: 1-20μs

Output: +3 to +13dBm; 50ohm
Spurious Outputs: −70dBc
Phase Noise: −63dBc (0.5Hz-15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: $8,675.00*

PTS 1000

Range: 0.1-1000 MHz
Resolution: 0.1Hz-100KHz (opt)
Switching: 5-10μs

Output: +3 to +13dBm; 50ohm
Spurious Outputs: −70dBc (0.1-500 MHz), −65dBc (500-1000 MHz)
Phase Noise: −60dBc (0.5Hz−15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
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PTS x10

Range: 10 MHz band, selected decade 0.1-100 MHz
Resolution: 1Hz
Switching: 1-5μs
Phase Continuous: 2 MHz band, even or odd steps

Output: +3 to +13dBm; 50ohm
Spurious Outputs: −65/−60dBc (typ/spec)
Phase Noise: −70dBc (0.5Hz-15KHz)

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Feb 15, 1991
(received 3/11/91)

Prof. B. L. Shapiro
968 Elsinore Court
Palo Alto, Ca 94303

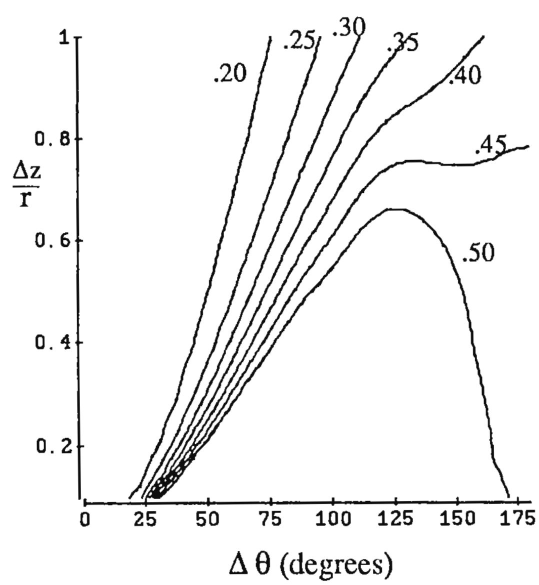
NOE Diffusion on Helices

Dear Barry:

In connection with our NMR studies of the structure of enzyme bound ATP we have theoretically investigated the NOE for several geometrical arrangements of spins[1,2]. Our intent has been to discover general features of magnetization transfer from analytical solutions of the multi-spin Solomon equations. We have found analytical solutions for molecules where the spins are symmetrically situated such as on a regular polygon, on a cubic lattice, or on a regular helix. One feature these solutions predict is the existence of a maximum range over which the magnetization may diffuse before decaying. This range depends both on the geometry and on the molecular (tumbling) correlation time. For strictly dipolar relaxation, the range R (in sites) is given by

$$R^2 = \frac{2\sum \alpha_k k^2}{\varepsilon \sum \alpha_k}$$

where α_k is the cross relaxation rate between spins k sites distant in the lattice, $\varepsilon = 6/(\omega\tau_c)^2$. ω is the Larmor frequency, and τ_c is the correlation time. The range formula essentially specifies which spins in a molecule will exhibit significant cross peaks in a NOESY experiment. Note the range becomes infinite for very large τ_c.



The ranges (R) of several *helical geometries* are displayed in the contour plot at the left. For each contour, $\log(R\sqrt{\varepsilon})$ is shown as a function of the helix rotation angle ($\Delta\theta$) between adjacent spins and the ratio of the translation along the helix axis between adjacent spins (Δz) to the helix radius (r). As an example, a slowly tumbling alpha helix ($\Delta\theta$ = 100°, $\Delta z/r$ = .6, ε=1.0) component in a macromolecule would have a diffusion range of about 3 sites, but for a similar *very* slowly tumbling structure (ε=.01) the range would be about 30 sites!

Sincerely,

Steve
Steven Landy

Dargu
B. D. Nageswara Rao

1. Landy and Rao, J. Magn. Reson. 83, 29 (1989).
2. Landy et al., J. Magn. Reson. 90, 439 (1990).

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February 26, 1991
(received 3/1/91)

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

TITLE: Bruker TAPE conversions on SGI systems

Dear Professor Shapiro:

Our NMR laboratory generates and stores massive amounts(1) of data from biological NMR experiments, and our medium of choice for archival is 9-track magnetic tape. We have linked our three Bruker spectrometers by Bruknet, and these systems are further linked by DECNet to our VAXs and by TCP/IP to two SGI computers -- one 4D25G and one 4D220. Through DECNet, we can ship datafiles throughout the company, and, in fact, can exchange data with our Japanese division quite rapidly. Even though we can shuffle the data everywhere, we still must face up to the problem of archiving it.

To this end, we have added a 6250/1600 bpi 9-track magnetic tape unit and Xylogics controller to the SGI 4D220 as a more efficient alternative to the Bruker tape system on the Aspect 3000. The Bruker tape unit is slow, and Bruker's TAPE program is very inefficient with regard to data density. My plan was to have users copy data from the spectrometers via Ethernet to the 4D220, process it there using FELIX, and/or archive as necessary at 6250 bpi on the SGI. We are just now getting Bruknet to work reliably to the SGI, and in the interim users continue to generate many tapes in the Bruker format. While tape-to-tape data transfer (SneakerNet?) is low tech, it is reliable and is still used regularly here.

I have written a program for the SGI that will read 1600 bpi Bruker-generated tapes and convert them to FELIX format. It is written in FORTRAN 77 using several VMS extensions available with the SGI compiler. It is composed of seven files and a Makefile that will generate the executable code. It includes subprograms for translating Bruker sixbit coding into normal ASCII, interpreting Bruker floating point into FORTRAN real numbers, and integer conversions. I am making this code available to anyone interested via electronic mail. Send requests to "72557.212@COMPUSERVE.COM". The program translates an entire tape of files to the corresponding files on disk with UNIX/FELIX compatible names. The user can then pick and choose from the disk, rather than tape. The code is free on an "as is" basis --no support!

Sincerely,

Paul Fagerness

(1) "massive amount" is defined as more than your disk space.

Department of Applied Physics
Faculty of Engineering, Hokkaido University
Sapporo 060, Japan
Tel. (011)513-2771 ext.6640
Fax. (011)726-4336

March 6, 1991
(received 3/11/91)

Professor Bernard Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Title: **Methyl group dynamics of poly(α-amino acid) by solid state ^{2}H NMR**

Dear Professor Shapiro:

A year has already passed since we can use Bruker MSL-200 at our Faculty. In this brief letter, we want to report some of solid state ^{2}H NMR data.

We made a probe insert for deuterium with 5 mm solenoid coil to fit a Bruker wide-line probe, because a pulse width was not enough in the company supplied insert. 90 degree pulse width with below 1.5 µs was accomplished in our insert, with the TX power controller value of 150.

We found the sample temperature to be quite different with the wide-line probe in the lower and higher temperature ranges, upon testing the BVT-1000 temperature controller unit. The temperature was calibrated with a digital thermometer with a thermocouple that had been placed near the coil. The difference between the front panel indicator of the BVT-1000 and the thermometer was found to be 5 to 25 degrees.

Figure 1 (a) and (b) show the quadrupole echo spectra of the deuterio methyl groups of poly(β-methyl L-aspartate) and poly(γ-methyl L-glutamate), respectively, as a function of temperature. Axially symmetric powder patters with the quadrupole splitting of 38 kHz were observed at below -40 °C for both samples, having the asymmetry parameter of nearly zero. Inspection of the inversion-recovery quadrupole-echo spectra show that the shoulders of the power patterns have about a half of T_1 of the singularities for spectra. These reveal the fast 3-fold jump reorientation of the methyl group about the C_3 axis.[1] With increasing temperature, both line shapes change significantly, suggesting additional motions with the rate of 10 kHz order of the C_3 axis, as well as the 3-fold jump motion.

we shall discuss the full story in a journal.

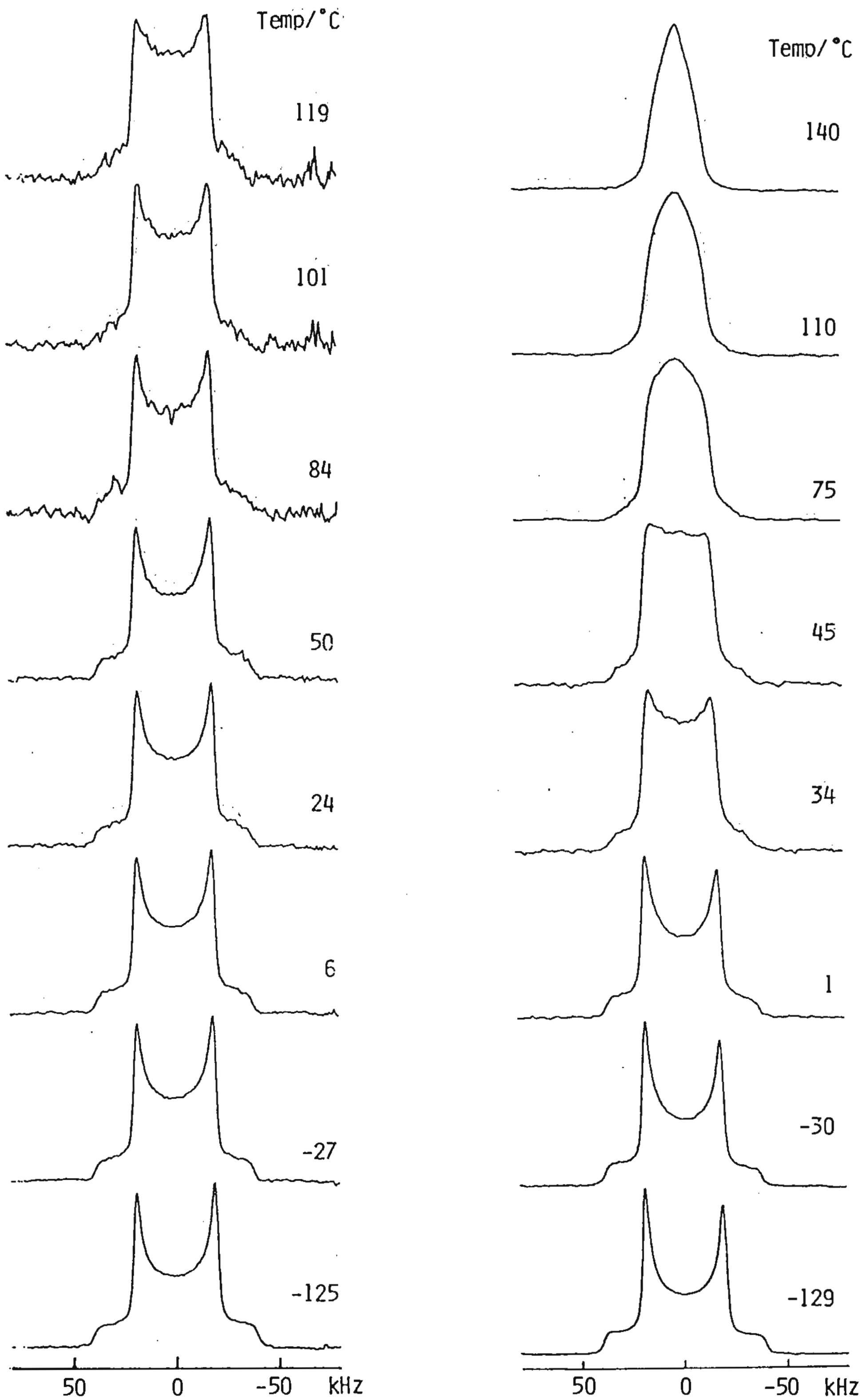
Sincerely

T. Hiraoki

Toshifumi Hiraoki

1) D.A. Torchia and A. Szabo, J. Magn. Reson., **49**, 107(1982).

Figure 1 (a) (b)


Temp/°C
119
101
84
50
24
6
-27
-125
50
0
-50
kHz
Temp/°C
140
110
75
45
34
1
-30
-129
50
0
-50
kHz

NMR Processing on a PC?

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Announcing Version 3 Release 2

About NMR-286

NMR-286 is a program that allows you to process 1D nmr spectra on an IBM PC-AT or PS/2 compatible microcomputer. Once a raw data file has been transferred to the PC's disk it can be read, windowed, Fourier transformed, plotted, integrated, its peaks fitted etc etc. NMR-286 is sophisticated enough that almost all of your routine (and many not-so-routine) nmr data processing needs can be done on a PC, away from the spectrometer. The command structure is much like that used by the nmr instrument manufacturers so that people with some experience in nmr processing will have little trouble in learning to use NMR-286.

Don't underestimate the power of your PC. Processing your spectra on your PC is practical. NMR-286 is written from the ground up for the PC, keeping both its weaknesses and its strong points in mind. It uses mixed high level and assembly language programming, efficient algorithms and an optimised overlay structure. Because of this, large data sets can be handled and the times taken for the various types of processing in NMR-286 are remarkably short.

NMR-286 gives you a full complement of functions to expand, examine, measure and do spectral arithmetic on your data sets. Instead of using knobs or mice to define the display regions and move the spectrum, NMR-286 uses the keypad for the these functions.

Features

- Lightning Fast FTs. An 8k Fourier transform takes about 16 seconds on a 6MHz 80286 based machine, 8 seconds on a PS/2 Model 50 and about 1 second on a 33 MHz 80386 based machine.
- Large Data Tables. Fourier transforms of data with sizes from 32 words to 32k words can be performed.
- Window Functions. Select from *Exponential*, *Lorentzian to Gaussian transformation*, *Sine Bell*, *Sin^2 Bell*, *Hanning* and three *Traficante* functions.
- Spectral Decomposition. Fit up to 30 peaks at once using a Marquardt-Levenberg fitting procedure. Parameters may be frozen or varied at will to allow inclusion of prior knowledge about the spectrum.
- Referencing. Use Absolute Frequency or Internal referencing.
- Parameter Menus. Parameters are entered in easy to use menus.
- Plotting. Plotting is extremely flexible. Send the HPGL output to a plotter, a file or a laser printer.
- Automated Processing. Almost anything that you can do from the keyboard, you can write a program to do. A powerful editor is a part of NMR-286.
- Interactive Spectral Expansion and Processing. The *Expand and Process* routine will, among many other things, allow you to
  - do sectional plotting
  - do baseline correction
  - do integration
  - do peak picking
  - compare two spectra in *Dual Display*
- Spectral Deconvolution. Rolling baseline caused by long pre-acquisition delays and the resulting large first order phase corrections can be removed.
- Manual. A comprehensive reference manual comes with NMR-286. It explains not only the commands used but also the ideas behind them.
- Public File Formats. NMR-286 uses a binary file format which is well described in the manual. It is also possible to import and export spectra as ASCII text files. Peak fitting results are stored as text files which can be read by popular spread sheets.

New in Version 3.2

- Marquardt Line Fitting Procedure. The simplex driven method has been replaced. The advantages are
  - much faster convergence
  - greater control over fitting
  - fitting statistics are available
  - possible inclusion of prior knowledge
- Support for the HP LaserJet III. A LaserJet III can serve as an economical output device which will serve as both the system's printer and plotter.
- Uses EMS if present. Can use Expanded Memory to reduce memory requirements and disk use.
- Spectral Arithmetic. Can add, subtract and scale spectra to produce, for instance, DEPT subspectra.

Hardware Requirements

* Computer: Required. A Personal Computer which conforms entirely to the IBM standard. The CPU must be a 80286, 80386 or i486. NMR-286 will not run on an 8086 or 8088 based PC. The operating system must be MS-DOS 3.0 or greater.
* Memory: 640k minimum required.
* Expanded Memory: Optional. If sufficient expanded memory is

present, the overlay will be loaded into memory thereby increasing performance.

* 80x87 coprocessor: Required. (Integral part of i486)

* Hard disk: *Very, very* highly recommended.

* High resolution graphics: EGA, VGA, Hercules and AT&T 400 line are all recommended.

* Serial ports: Optional. Depends upon configuration of peripherals.

* Printer: Optional.

* Plotter: Optional. NMR-286 supports the HP 7440 (Color Pro) graphics plotter, the 7470, the 7550 and will probably support any other plotter that uses HPGL plotter instructions. The HP LaserJet III is now completely supported and will serve as both the plotter and printer. A memory upgrade of 2 Mbytes is recommended for the LaserJet III.

Spectrometers Supported

NMR-286 is in itself independent of the spectrometer. It just as happily processes data from any spectrometer. It requires, however, a translation program to convert the data files to NMR-286 format. Currently such programs exist for Bruker DISNMR, DISCXP, DISMSL and AMX files as well as for Lybrics format files. Have another type of machine? Call!

File Transfer

The Kermit package is included at no extra charge with NMR-286 and may be all you need. However, NMR-286 is compatible with any method which transfers a file in tact.

Upgrade from 3.1

Present NMR-286 users can receive an upgrade to Release 2 for a shipping and handling fee of $50.00. Contact SoftPulse for more information.

Software Support

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NMR-286 Prices

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1	1500.00
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Coprocessors

SoftPulse now handles coprocessors for PCs. These are easily installed by the user and will improve the performance of any software that supports or requires one. For 80286 computers we carry the Intel 80287XL. One chip is used for all clock speeds up to 12 MHz. For 386 based machines we handle the Cyrix line. These are 100% compatible with the Intel chips but give much better performance at lower prices. Some Cyrix features:

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- Transcendental functions computed with greater accuracy

- Low power consumption – 30% of the 80387, great for laptops

- Fully pin and software compatible with the 80387

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Cyrix	
CX83X87-16 for 386SX-16	373.75
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CX83D87-16 for 386DX-16	460.00
CX83D87-20 for 386DX-20	506.25
CX83D87-25 for 386DX-25	618.75
CX83D87-33 for 386DX-33	775.00

All prices are in Canadian dollars. Canadian orders add 7% GST, Ontario orders add 8% PST. Academic institutions are eligible for a 33% discount on software. Purchase orders accepted. Shipping per order: Canada – $15.00, elsewhere $30.00. Foreign orders may be paid in the equivalent of U.S. dollars.

NMR-286 will help you use your valuable magnet time for acquiring data. You can process, examine, measure and plot your spectra when and where you want — in the lab, in your office or at home. Try it, you'll like it. You can even try it ***Risk Free***! Buy NMR-286 and if within 30 days you decide that NMR-286 is not for you, your purchase price will be refunded. Questions? Call, fax or write.

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The University of Melbourne

School of Chemistry
February 11, 1991
Parkville, Victoria 3052

Dr. Barry L. Shapiro
Editor, TAMU Newsletter
California

NMR Studies and Conformational Analysis of Cyclic Peptides

(received 2/20/91)

Dear Barry,

We have recently been examining the conformation of some small oligopeptides in solution on our JEOL GX400 spectrometer. One such example is the Cyclo(Boc-lys-lys-OBu^t), **1**, obtained via the coupling reaction of two lysine side-chains with carbonyldiimidazole as the cyclization reagent (based on Ph.D. thesis of Dr. A. M. Bray).

Our ^{1}H assignments were made using a combination of phase-sensitive DQF-COSY, relayed COSY and 1D NOE difference techniques. However, the relatively short T_2's make it difficult to fully assign the well-dispersed ^{13}C resonances by the standard HETCOR, H-relayed C,H and COLOC experiments.

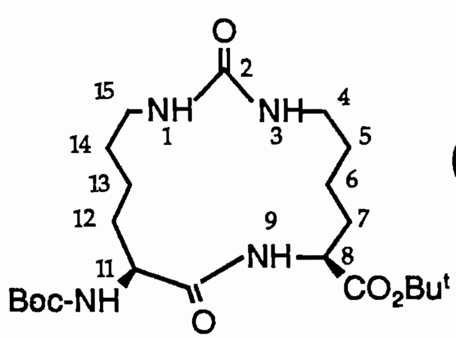
The conformational preference of this macrocycle was deduced from model building studies, consideration of the solvent accessibilities and chemical shift values of the NH protons, and a series of 2D NOESY and 1D NOE difference experiments. Only two conformers were considered likely on the basis of CPK model building experiments: conformers **1A** and **1B**. The observation of both positive and negative NOE's provides evidence for the linearity C(8)-N(9)-C(11) system which is indicative of conformation **1B**. Further 2D work on medium-size oligopeptides is in progress.

Sincerely,

T. K. Lim   D. P. Kelly

Proton irradiated	Proton observed						
	7-H$_A$,%	7-H$_B$,%	8-H,%	9-H,%	11-H,%	BocN-H,%	12-H,%
BocN-H				5.8	4.5		(+ve)*
9-H		3.0	5.7		5.7	6.6	
8-H	4.0	1.3		**2.7**	**-2.7**		
11-H			**-0.8**	**2.0**		1.7	6.3

* Integration was not carried out.



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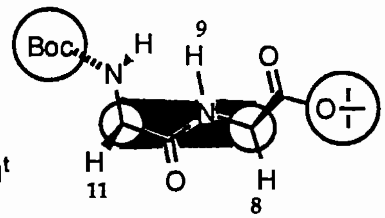
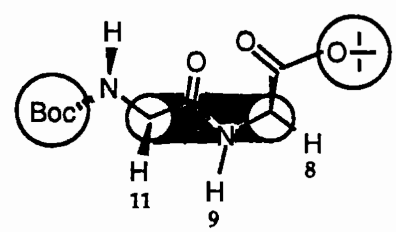


1A



1B

NMR SPECTROSCOPIST

The DuPont Merck Pharmaceutical Company has an opening in its Chemical Sciences Department for a PhD Level NMR Spectroscopist with a strong background in organic chemistry. The position will involve the structural characterization of pharmaceutical candidates and their metabolites. Particular emphasis will be placed on collaborative studies with synthetic/medicinal chemistry. Good written and oral communications skills are needed as is the ability to work well with other people.

NMR facilities include four Varian VXR/Unity 500s, a VXR-400 and a three-channel Unity-400. These are part of an evolving large scale, instrument/computer network. A VXR-500 and two Bruker AMX-600 instruments are also available on-site. Computational facilities include a variety of Silicon Graphics devices, a substantial VAX cluster and the Cray-Y/MP super computer.

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A partnership of the Du Pont Company
and Merck & Company, Inc.

Interested parties should send a curriculum vitae and names of three references to: John M. Read, The DuPont Merck Pharmaceutical Company, Experimental Station E353/7, P.O. Box 80353, Wilmington, DE 19880-0353.

Position Available
NMR Scientist

NCC

Nalorac Cryogenics Corporation has an immediate opening for an NMR Scientist at our Martinez, California corporate headquarters. The position is in the Z•SPEC Probe Division. The Z•SPEC Probe Division is responsible for the design, development, and manufacture of NMR probes.

The ideal candidate should have a BS or MS in Chemistry, Physics or a related field plus a working knowledge of NMR hardware and software. Candidates with a knowledge of electronics and computers, along with a desire to learn NMR spectroscopy should not be discouraged from applying.

Interested applicants should send their resume to Dennis Sandoz,

Nalorac Cryogenics Corporation,
837 Arnold Drive, Suite 600, Martinez, CA 94553.

UNILEVER RESEARCH LABORATORY

Postdoctoral position in protein NMR spectroscopy

THE TENTH ANNUAL SCIENTIFIC MEETING OF THE SOCIETY OF MAGNETIC RESONANCE IN MEDICINE will be held at the San Francisco Hilton and Towers, San Francisco, California, August 10-16, 1991. Weekend Educational Programs will be held on August 10 and 11. The scientific sessions begin on August 12. Further information may be obtained from the Society of Magnetic Resonance in Medicine, 1918 University Avenue, Suite 3C, Berkeley, CA 94704, USA. Telephone: (415) 841-1899, Fax: (415) 841-2340.

391-56

Faculté des sciences

UNIVERSITÉ DE SHERBROOKE

Sherbrooke (Québec) Canada J1K 2R1

March 12, 1991
(received 3/18/91)

Volume Magnetic Susceptibility of a Two-Component One-Phase System

Dear Dr. Shapiro,

In a two-component one phase system the volume magnetic susceptibility is given by a weighted average of each component's contribution. For a mixture of diamagnetic substances, this approximation is known as the Wiedemann's additivity law and is represented by

$$\chi_V = \phi_1\chi_{V1} + \phi_2\chi_{V2}$$

where χ_v is the volume magnetic susceptibility of the mixture, χ_{vi} the susceptibility of pure component i, and ϕ_i is the volume fraction of the i^{th} component. With such a sample in a cylindrical tube oriented parallel to the solenoid axis in a superconducting magnet of field strength H_o, the effective magnetic field H_e is given by

$$H_e = H_o\left[1 + \left(\frac{4\pi}{3}\right)\left(\phi_1\chi_{v1} + \phi_2\chi_{v2}\right)\right]$$

The variation in the effective field ΔH_e due to the variation in the volume fraction $\Delta\phi_1$ gives

$$\frac{\Delta H_e}{\Delta\phi_1 H_o} = \frac{\Delta\delta}{\Delta\phi_1} = \left(\frac{4\pi}{3}\right)\left[\chi_{v1} - \chi_{v2}\right]$$

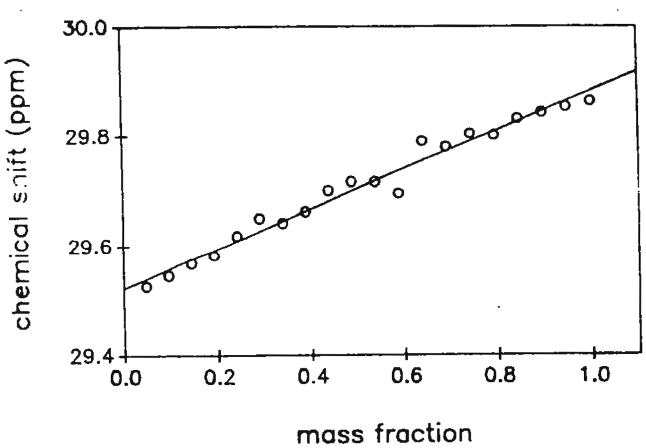
where $\Delta\delta$ is the chemical shift variation due to changes in its volume fraction. Knowing the molar magnetic susceptibilities, molecular weights, densities of the components, and assuming the additivity of molar volumes permits to predict the slope of the chemical shift of component 1 as a function of its mass fraction. For the binary mixture, cyclohexane/aniline, such a calculation yields an expected slope of 0.32±0.04. In Figure 1, the chemical shift variation of the ^{13}C resonance of cyclohexane in this mixture as a function of its mass fraction gives 0.357±0.016. This approach has been used to monitor the effects of macroscopic flows on the composition fluctuations in a two-phase two-component system (S. Lacelle, F. Cau, and L. Tremblay (submitted)).

S L — Serge Lacelle

Franco Cau

L.T. — Luc Tremblay

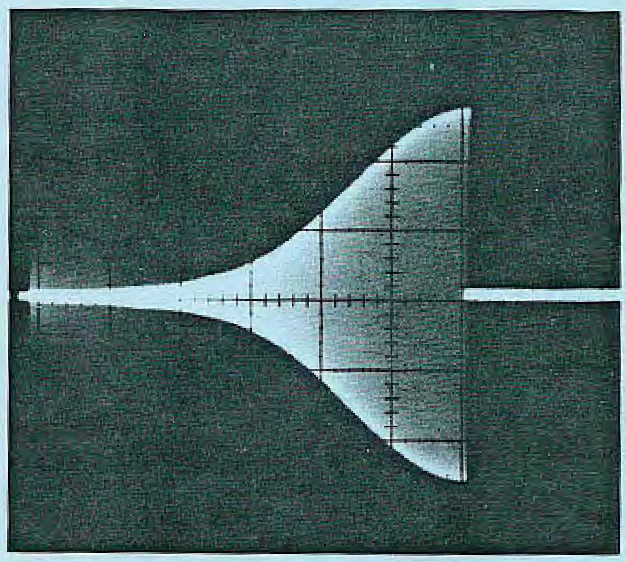
Fig. 1 →
T= 34°C



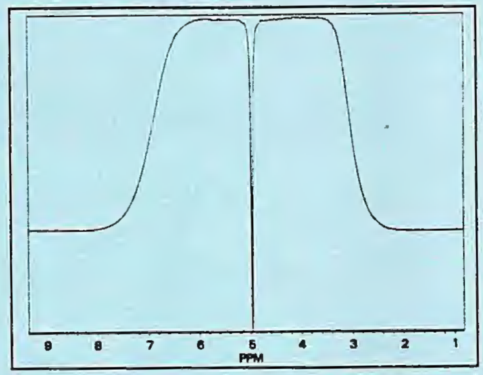
Omega
Pulse Shaping Made Simple

Omega PSG (Pulse Sequence Generator) boards provide very flexible control of both amplitude and phase on each transmitter channel. Through a unique combination of instruction and waveform memory, waveform libraries can be easily created by the user. Normalized waveforms can be recalled and modified in amplitude or duration by a single instruction resulting in very efficient pulse programs.

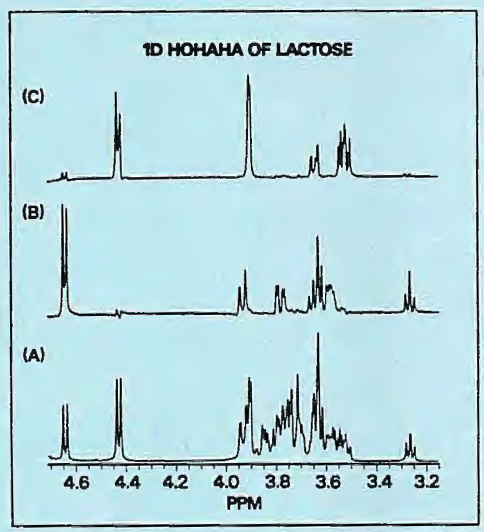
Wave Shaping on the Omega 500 PSG



An oscilloscope trace of a half-Gaussian pulse. The pulse is defined by 250 points and the duration is 10 ms.



The result of applying a 180° half-Gaussian pulse to a sample of doped water. The water resonance has been broadened by introducing a large Z1 current in the room temperature shims. The half-Gaussian pulse width is 200 ms and the width of the "burned hole" is 12 Hz.



TOCSY of Lactose (10mM in D_2O).
Bottom spectrum (A) is a simple one pulse spectrum. Middle spectrum (B) is a 1D-TOCSY spectrum, where anomeric proton at 4.43 ppm has been selectively irradiated with a half-Gaussian pulse. Top spectrum (C) is a 1D-TOCSY spectrum when the anomeric proton at 4.65 ppm has been selectively irradiated with a half-Gaussian pulse.

GE NMR Instruments

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