TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 399

December 1991

Continued on page 2

TABLE 1 DEUTERATED SOLVENTS

Cat. No.	Description	Formula	Min. Isotopic Purity (D)	Density (g/cc)	MP (°C)	BP (°C)	$-\chi_v \times 10^6$ @ (°C)
D-11	Acetic Acid-d_4	CD_3COOD	99.5%	1.12	17	118	0.551 (32)
D-120	Acetic Acid-d_4 + TMS						
D-13	Acetone-d_6	CD_3COCD_3	99.8%	0.87	-94	57	0.460 (20)
D-121	Aceonte-d_6 + 1% TMS		99.8%				
D-129							
D-14							543 (20)
D-21							0.611
D-122							
D-130							
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])	11" X 26"	[illegible]	Gridded-Two Color
WCV-XLFT-100	11" X 26"	XL-100 (C 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" X 17"	CFT-20, FT-80, FT-80A All Models [illegible]	Gridded-Two Color 16 1/2" or 16 Blank

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FORTHCOMING NMR MEETINGS

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

33rd ENC (Experimental NMR Conference), Asilomar Conference Center, Pacific Grove, California, **March 29 - April 2, 1992**; Contact: ENC, 750 Audubon, East Lansing, MI 48823; (517) 332-3667

Sixth Washington University-ENI/Emerson Electric Co. Symposium on NMR, St. Louis, Missouri, **May 18, 1992**; Contact: Karen Klein, Wash. Univ.; (314) 935-6405.

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.

XV International Conference on Magnetic Resonance in Biological Systems, Jerusalem, Israel, **August 16 - 21, 1992**; Contact: Prof. Gil Navon, XV ICMRBS, P. O. Box 3190, Tel Aviv 61031, Israel.; Tel. (972-3) 5271111, Fax: (972-3) 5239099.

High Resolution NMR Spectroscopy (a residential school), University of Sheffield, England, **April 1993**[*sic*]; Organizer: Dr. B. E. Mann (Sheffield); For information, contact Ms. L. Hart, The Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, England; Tel.: 071-437-8656.

Additional listings of meetings, etc., are invited.

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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. 401 (February) --------- 24 January 1992
No. 402 (March)----------21 February 1992
No. 403 (April) ----------20 March 1992
No. 404 (May) ----------24 April 1992

Dear Colleagues:

Each year during the holiday season we pause to reflect on the year gone by and the year to come. We are grateful to you, the NMR community, for your continued support and confidence in Doty Scientific and our products.

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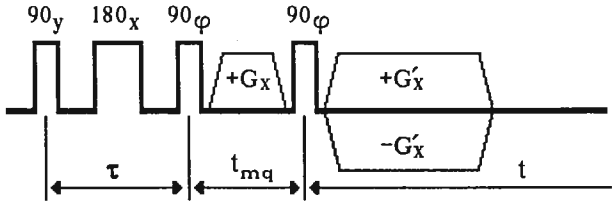
Prof. B. Shapiro
Tamu NMR Newsletter
966 Elsinore Court
Palo Alto CA 94303 USA

(received 10/26/91)
October 10, 1991

Selection of sodium double and triple quantum coherences by gradients and phase-cycling.

Multiple quantum (MQC) filtering in combination with a relaxation reagent (1) may be a useful tool to separate intra- and extracellular in vivo sodium signals. However, multiple step phase-cycled MQC filtering is hampered in vivo by movements of the object. Therefore we investigated single shot selection of 2QC's and 3QC's by gradient pulses using the pulse sequence:



To select the 2QC: φ is set to y and G_x' to $2\times G_x$. To select the 3QC: φ is set to x and G_x' to $3\times G_x$. Using straight forward density matrix calculations the selected in vivo MQC without gradients is given by:

$$M_t(t) = \frac{1}{5} M_0 \left(e^{\frac{-\tau}{T_s}} - e^{\frac{-\tau}{T_f}}\right) f(n,\omega,t_{mq}) \left(e^{\frac{-t}{T_s}} - e^{\frac{-t}{T_f}}\right) e^{i\omega t} \quad (1)$$

$M_t(t)$ is the transverse magnetization, T_f and T_s the fast and slow transverse relaxation constants (2,3), ω the offset frequency, τ the preparation time, t the acquisition time, and $f(n,\omega,t_{mq})$ is a function which describes the behaviour of the signal during the MQC evolution time t_{mq}.

$$f(n,\omega,t_{mq}) = \frac{3n}{8} e^{\frac{-t_{mq}}{T_{nqc}}} \left(e^{in\omega t_{mq}} + e^{-in\omega t_{mq}}\right) \quad (2)$$

T_{nqc} is the multiple quantum relaxation constant, (n=2 for the 2QC and n=3 for the 3QC). The positive or negative MQC component is refocussed, depending on the sign of G_x'. So a factor of two in signal is lost compared to phase cycling techniques, where a $\cos(n\omega t_{mq})$ modulation results. There are three advantages of the 3QC over the 2QC: 1) the larger amplitude of the 3QC, 9/8 compared to 6/8 for the 2QC amplitude, see also ref 4; 2) the smaller 3QC relaxation rate, $T_{3qc} = T_s$ and $T_{2qc} \approx T_f$, see ref 2,3; 3) G_x' dephases better the unwanted 1QC, and allows therefore a

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shorter G_x than t_{mq} for the same suppression. In the figures the absolute value mode signal as a function of t_{mq} is shown for a BSA/NaCl aqueous solution at 4.7T, offset frequency 400 Hz. The gradient strength was 50 mT/m, apllied for 1 ms for G_X and 2 or 3 ms for G'_X. In Fig. 1 the cosine modulation is absent in the gradient selection experiment. The decay of the signal as a function of t_{mq} is besides the effect given in eq (2) also affected by B_0 inhomogeneity. Only the inhomogeneity dephasing of the MQC's during G_x is compensated when a positive G'_x is applied. This accounts for the faster decay of the negative G'_x selected MQC's. The cosine modulation of the gradient selected MQC's at half the frequency of the phase-cycled 2QC is due to partly unsuppressed 1QC's. These are stronger suppressed in the 3QC experiments in fig. 2. The suppression seems sufficient for in vivo applications. Non linear model fitting of the measurements gave a T_s of 13.9 ms and a T_{2qc} of 6.1 ms close to the T_f of 6 ms. The field inhomogeneity hampered the fit of the 3QC relaxation constant but in fig. 2 the slower relaxation of the 3QC as compared to the 2QC relaxation is visible.

References

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2. Jaccard G., Wimperis S., Bodenhausen G., J. Chem. Phys. 85,6282,1986.
3. Rooney W.D., Barbara T.M., Springer C.S. Jr., J. Am. Chem. Soc. 110,674,1988.
4. C.W. Chung, S. Wimperis, J. Mag. Reson. 88,440,1990.

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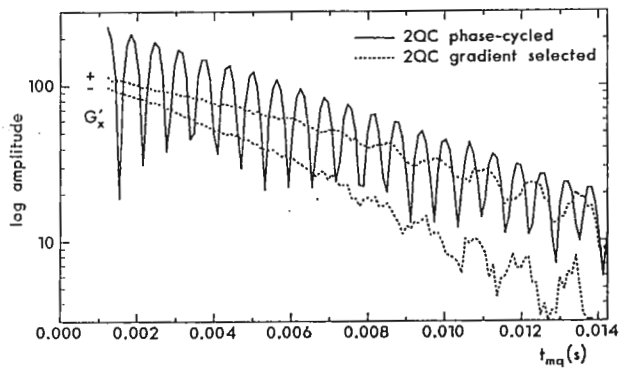

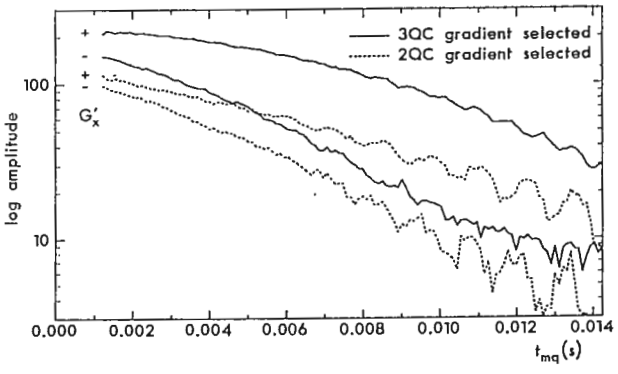

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(received 11/13/91)

A Simple Method to Produce Sharp Multiple Slice Irradiation.

Tagging by multiple stripes or a grid has been used for looking at heart wall motion (1,2). It has also been used for flow imaging by bolus tracking (3) and mapping flow streamlines (4). The method is adaptable to most imaging sequences by the addition of saturating radio frequency (rf) pre-pulses for tagging and it is attractive because motion is mapped by the displacement of stripes on standard magnitude images.

Several different approaches have been used for tagging; by radial stripes (1), 1-3-3-1 or 1-4-6-4-1 pulses (2), DANTE pulses (5), and modification of sinc pulses (3,4). In this letter we show how any selective rf irradiation can be replicated in the frequency domain so that it becomes a multiple selective excitation.

If S(t) is a selective rf pulse then we construct the striping pulse R(t) by zeroing S(t) over regularly spaced intervals. Thus

$$R(t) = \begin{cases} S(t), & \text{for } kT - A \le t \le kT + A, \text{ for all } k \\ 0, & \text{otherwise.} \end{cases}$$

The function R(t) can be contructed easily from the digital form of S(t) by skipping points at regular intervals. If we define a function $f(t) = 1$ for $|t| \le A$ and zero otherwise, then

$$R(t) = S(t)\Sigma\, f(t + kT).$$

The Fourier transform of R(t) is a given by

$$R(\omega) = F(\omega)\ \Sigma\ S(\omega + 2\pi k/T),$$

where $F(\omega)$ and $S(\omega)$ are Fourier transforms of f(t) and S(t) respectively. The small tip angle approximation gives the slice profile excited by R(t) to be $R(\omega)$, with $\omega = \gamma Gx$, where G is the magnetic field gradient applied during the rf pulse. The distance between the stripes is given by $X_s = 2\pi/(\gamma GT)$. The profile of each stripe is determined by $S(\omega)$, while $F(\omega) = 2A\sin(\omega A)/(\omega A)$ modulates the periodic striping function $\Sigma\ S(\omega + 2\pi k/T)$. The region of effective stripes is limited by the shape of $F(\omega)$. The shape of each stripe is $S(\omega)$ which is determined by S(t). The sharpest stripe we have used is with $S(t) = \sin(at)/at$.

An example of stripes in a water filled pipe with 2.54 cm i.d. and a 8 mm circular orifice is shown in Fig. 1. We have used $S(t) = \sin(at)/at$, for $t \le L$ and $a = 5\pi/L$, where $L = 8192$ μs. This pulse was sampled 256 times to give a dwell time per sample to be 64 μs ($\equiv 2A$) and 5 points were skipped to give $T = 320$ μs. The gradient was adjusted to give a stripe separation of 5 mm and the

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frequency offset of the rf pulse adjusted to place one stripe through the center of the orifice. The image on the left is without the striping pre-pulse and on the right with the stripes.

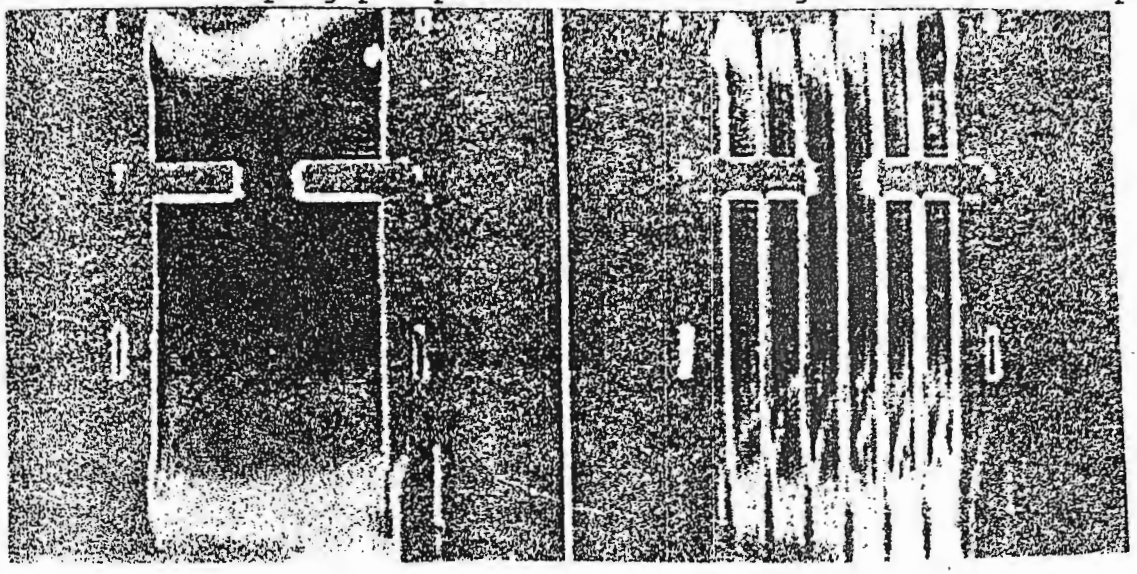

Fig. 1

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(received 11/7/91)

Re: **NMR Assignments of Alkylcyclopentadienyl Ligands in a Zirconium Complex Using Long-range Heteronuclear Correlation Techniques**

Dear Barry:

A recent publication[1] illustrated NMR methods leading to the unambiguous assignment of the ^{13}C NMR spectra of alkylcyclopentadienyl ligands, with particular attention directed towards the carbons α and β to the alkyl substituent. This publication used the INADEQUATE technique and homonuclear nOe measurements, as well as information gleaned from homonuclear and heteronuclear coupling constants to fully assign a series of zirconium and platinum alkylcyclopentadienyl complexes.

For the complete assignment of the ^{1}H and ^{13}C spectra of the zirconocene complex $(MeCp)_2Zr(Cl)_2$, (**I**), examined here, as well as other related complexes, a combination of normal heteronuclear and long-range heteronuclear correlations should prove sufficient. The ^{13}C NMR spectrum of **I** contains signals at 117.51 and 112.29 ppm due to the α and β cyclopentadienyl methine carbons. The ipso carbon resonates at 130.22 ppm and is readily identified by its low intensity relative to the methine signals. The methyl resonates at 15.53 ppm and is easily identified by its heteronuclear correlation with the proton singlet at $\delta_H = 2.26$ ppm.

Of the numerous long-range heteronuclear correlation experiments cited in the literature the XCORFE sequence of Reynolds *et al.*[2] is generally utilised within this department. Figures 1 and 2 show the HETCOR and XCORFE spectra respectively obtained for **I**. Examination of the XCORFE spectrum shows a two- and three-bond correlations from the methyl protons to the ipso carbon and to the α-carbon respectively. The remaining methine carbon may therefore be assigned to the β-carbon, and the associated proton resonances may therefore be assigned from the HETCOR spectrum ($\delta_\alpha{}^H = 6.17$ ppm, $\delta_\beta{}^H = 6.26$ ppm). These assignments verify the ordering of the given by Newmark *et. al.*[1] with the α-carbon resonating to low-field of the β-carbon, and also confirms the utility of long-range heteronuclear experiments in the assignment of alkylcyclopentadienyl and related complexes.

1. Newark, R.A.; Boardman, L.D; Seidle, A.R.; *Inorg. Chem.* **1991**, *30*, 853
2. Reynolds, W.F; Hughes, D.W; Perpick-Dumont, M; Enriquez, R.G; *J. Magn. Reson.* **1985**, *63*, 413

Yours sincerely,

A.J. Williams

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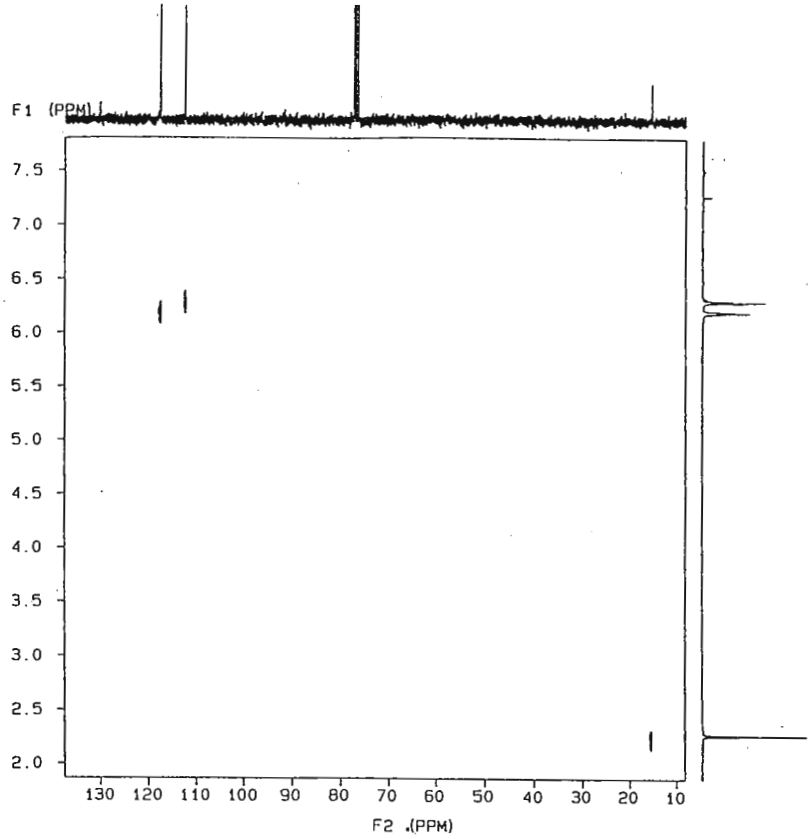

Figure 1 : ^{13}C-^{1}H heteronuclear correlation spectrum of $(MeCp)_2Zr(Cl)_2$

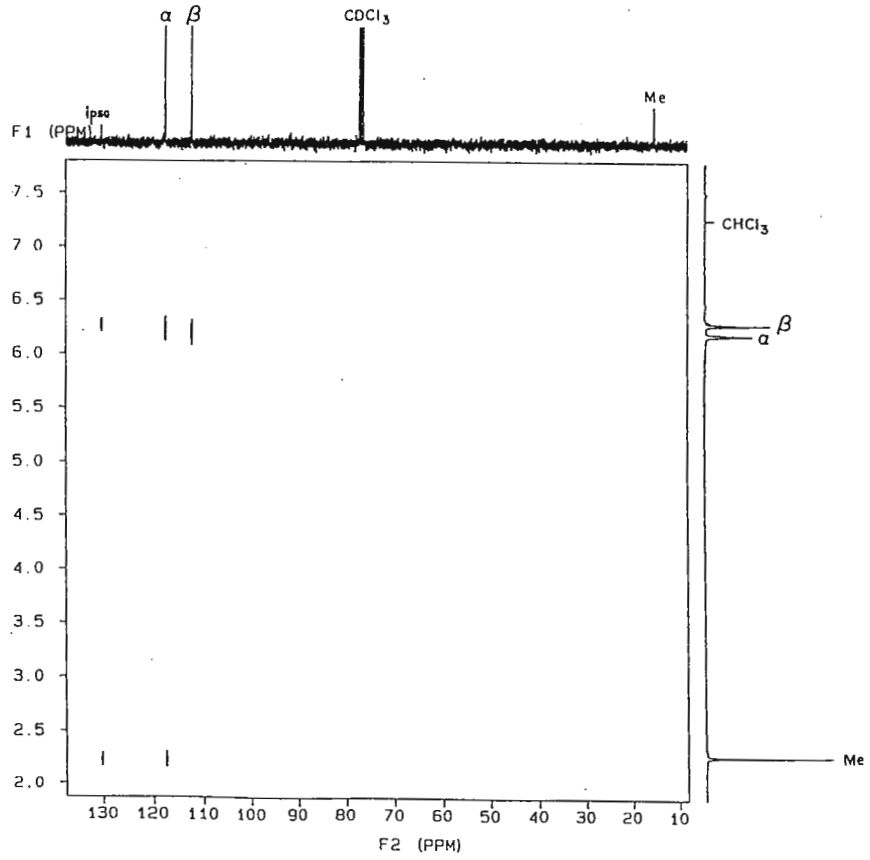

Figure 2 : ^{13}C-^{1}H Long-range heteronuclear correlation (XCORFE) spectrum of $(MeCp)_2Zr(Cl)_2$

The College of Staten Island

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STATEN ISLAND, NEW YORK 10301

October 30, 1991
(received 11/4/91)

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

Looking at Fatty Multilayers

Dear Barry:

In the course of ^{13}C NMR studies on phosphatidylcholine - triolein (PC-TO) multilayers, a number of trends have emerged regarding how to look at these spectra and what may be learned from them.

1. The combination of magic-angle spinning (MAS) and high-power decoupling (DD) suffices to produce high-resolution spectra for these model digestive mixtures (Figure 1). Motion in the liquid crystals makes cross polarization superfluous and/or inefficient; lines are sometimes fully narrowed with spinning speeds as low as 500 Hz and decoupling fields of just 6 kHz or so. Both chemical shifts and peak integrals in the mixtures are as predicted from spectra and compositions, respectively, of the individual constituents.

2. **Changing the spinning rate** usually has no impact on linewidths for spectra obtained with the MASDD experiment, but the value for CHO backbone carbons in egg PC multilayers actually drops from 70 to 43 Hz when υ_R is dropped from 2000 to 500 Hz at our field of 4.7 T. Any explanations, friends?

3. **Lowering the decoupling strength** (from about 50 kHz to 5 kHz) produces site-specific changes that reflect molecular organization in these aggregates: (a) all peaks are broadened significantly in egg PC multilayers, reflecting the rigidity (and/or order) of the liquid crystal; (b) resonances of the acyl-chain carbons are broadened even in a neat triolein oil, so motional averaging must be incomplete; (c) linewidth variations in a 3PC:1TO dispersion indicate that formation of mixed-lipid multilayers enhances fluidity (disorder) of all acyl chains but restricts the motions (promotes order) of the PC glycerol backbone (Figure 2).

4. ^{1}H NMR and MAS-assisted NOESY are quite feasible in these mixtures, though their structural interpretation is a more complex and subtle exercise...

Very truly yours,

Ka-loh Li

Ruth

Ka-loh Li
Postdoctoral Research Associate

Ruth E. Stark
Associate Professor of Chemistry

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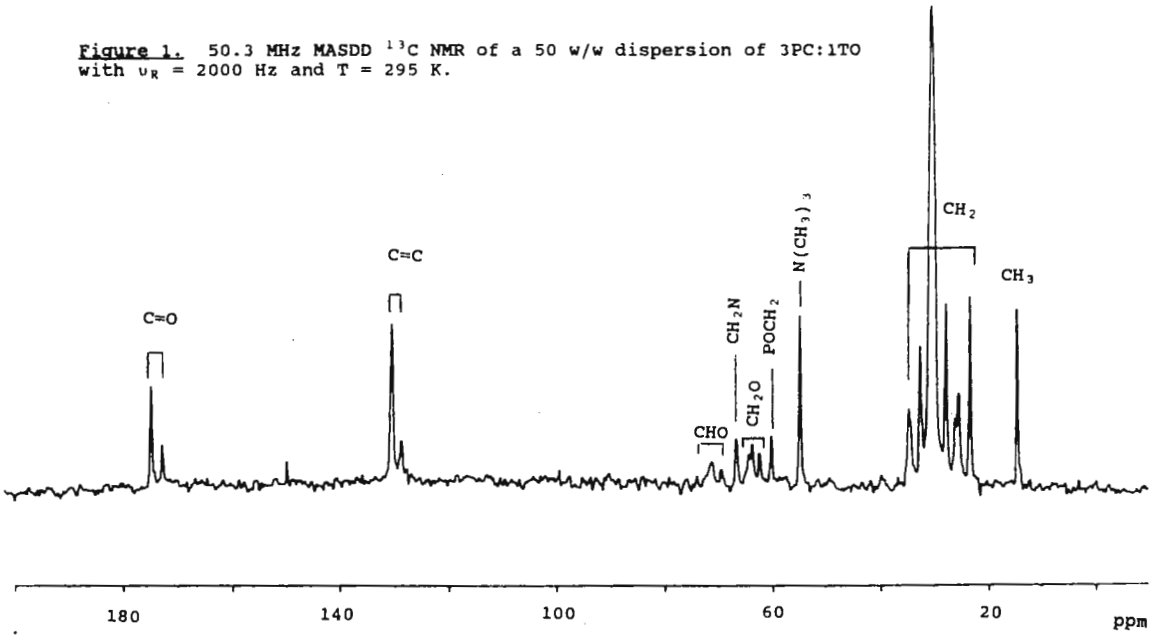


Figure 1. 50.3 MHz MASDD ^{13}C NMR of a 50 w/w dispersion of 3PC:1TO with υ_R = 2000 Hz and T = 295 K.

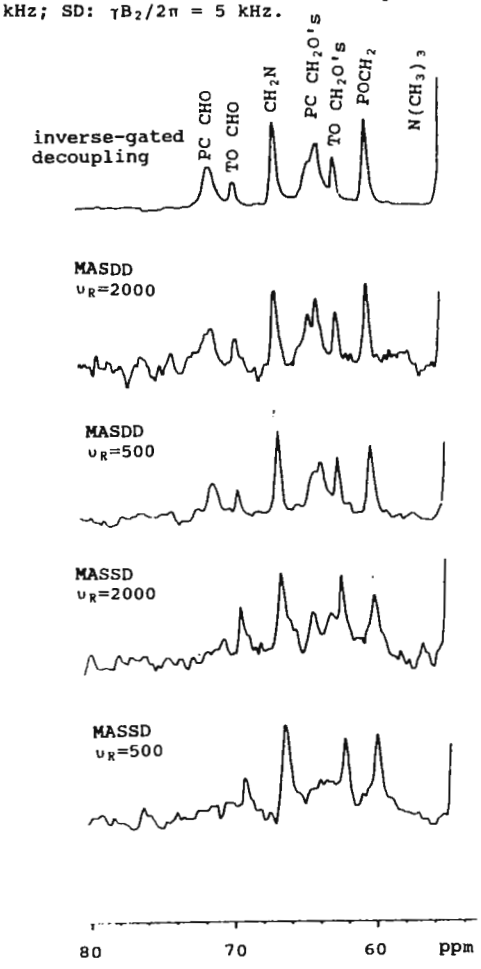
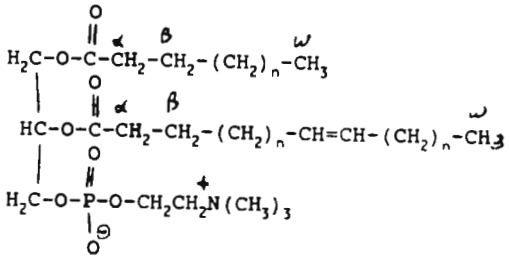
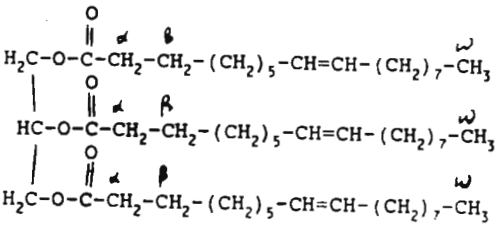


Figure 2. MAS ^{13}C NMR of the backbone and headgroup region of a 3PC:1TO mixture under various acquisition conditions. DD: $\gamma B_2/2\pi$ = 50 kHz; SD: $\gamma B_2/2\pi$ = 5 kHz.

The chemical structure of eggpc



The chemical structure of triolein



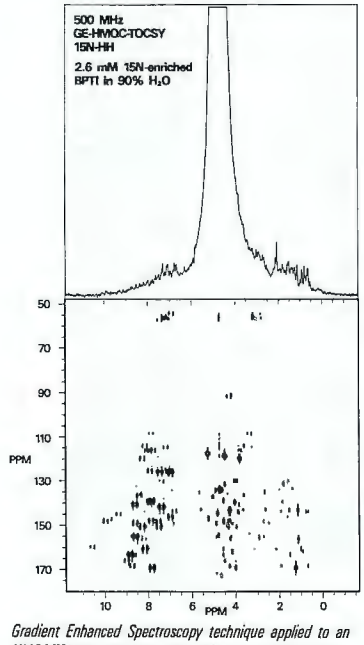
NMR UPDATE

Gradient Enhanced Spectroscopy: a new, practical answer

By Frank Huang, PhD, Paul Calderon, MS, and Boban John, PhD

Making Gradient Enhanced Spectroscopy (GES) a viable method for high resolution spectroscopy has long been of interest to researchers. The obvious benefits in speed and information content were too often overshadowed by the drawbacks of signal loss and distortion.

Technology developed at GE NMR Instruments has overcome these challenges. The S-17 Gradient Enhanced Spectroscopy Accessory with integrated inverse probehead makes GES practical for a broad range of applications in 1D, 2D, 3D and 4D experiments.



Gradient Enhanced Spectroscopy technique applied to an HMQC-TOCSY experiment demonstrates excellent water suppression without the need for presaturation or selective excitation.

Research Implications

- Speed without phase distortion or signal loss.
- Practical for 1D, 2D, 3D and 4D experiments.
- Accommodates proton and heteronuclear GES techniques.

A better design

The use of a three-axis, actively-shielded gradient set allows GE to overcome the inherent drawbacks of previous GES technology —most notably, phase distortion and signal loss:

Active shielding. Eddy current effects are the major source of phase distortion in GES spectra. Active shielding prevents interaction of strong gradients with magnet and shim components—the source of eddy current effects.

Fast, strong gradients. Short gradient pulses in excess of 20 G/cm minimize signal loss during pulse sequences.

Applications advantages

With its integral inverse probehead, the S-17 Accessory can accommodate proton as well as heteronuclear GES techniques.

Gradient fields in excess of 20 G/cm are able to suppress water in aqueous samples and to improve performance in heteronuclear experiments. Other applications advantages:

- Eliminates phase cycle requirements and subtraction error.
- Reduces T1 noise.
- Reduces collection times for 2D, 3D and 4D data sets.
- Provides lineshape independent water suppression in multiple quantum coherence selection experiments.
- Provides lineshape independent water suppression via diffusion differences for large molecular weight samples.
- Improves water suppression in experiments using selective time reversal RF pulses.
- Separates cross-correlation and exchange phenomena in NOESY experiments.
- Distinguishes chemicals inside the cell from those outside in whole cell applications.

For additional information on the S-17 GES Accessory, write to GE NMR Instruments, 255 Fourier Ave., Fremont, CA 94539.
Or call toll free:

1-800-543-5934

GE NMR Instruments

Gradient-Enhanced ^{15}N HMQC

The pulse sequence and the coherence pathway diagram for a ^{15}N GE-HMQC are shown in Fig. 1. The pulse sequence was a standard ^{13}C GE-HMQC experiment (l) with different gradient amplitudes to account for the difference between the gyromagnetic ratios of ^{13}C and ^{15}N. The 90° proton pulse creates transverse magnetization which evolves into an anti-phase state with respect to J(NH) coupling at the end of the period Δ (where Δ = ½J (NH)). The antiphase components are converted into heteronuclear zero- and double-quantum coherence by the ^{15}N 90° pulse and the multiple quantum coherences are allowed to evolve during t_1. The 180° ^{1}H pulse in the center of the evolution period serves to eliminate the ^{1}H chemical shift evolution, yielding pure ^{15}N chemical shifts along that axis. The zero- and double-quantum signals are then *coherence-order labeled* by the gradient pulses G1 and G2. After conversion into antiphase proton magnetization by the last ^{15}N 90° pulse, the desired components are refocused by the gradient G3 and detected. The application of a gradient pulse results in a phase factor being applied to the magnetization which is dependent upon gradient strength, duration, the distance from the gradient isocenter, the gyromagnetic ratios of the coupled nuclei, and the desired coherence order. The relative amplitudes of the labeling and refocusing gradient pulses will determine the selection of a specific coherence pathway and are calculated to suppress magnetization components arising from the solvent and other protons not coupled to ^{15}N spins.

The fundamental principle of coherence selection using gradients is that for a pathway to be detected, the cumulative phase factor during the acquisition must be zero:

$$G_1p'1 + G_2p'_2 + G_3p'_3 = 0. \qquad [1]$$

The subscripts denote steps in the pulse sequence where p′ defines a composite coherence order for the heteronuclear case which includes the gyromagnetic ratios of the coupled nuclei:

$$p' = {}^{p1}\mathrm{H} + (\gamma^{15}\mathrm{N}/\gamma^{1}\mathrm{H})^{p15}\mathrm{N} \qquad [2$$

and ^{p1}H and ^{p15}N are the coherence orders for the ^{1}H and ^{15}N spins respectively.

In the coherence pathway diagram, the relevant values of p' are given to the left and the relative gradient areas (gradient strength x duration) are given next to each gradient pulse. The following pathway (shown in *Fig. 1*):

$$\mathrm{H}(+1)\rightarrow \mathrm{H}(+1)\mathrm{N}(0)\rightarrow \mathrm{H}(+1)\mathrm{N}(+1)\rightarrow \mathrm{H}(-1)\mathrm{N}(+1)\rightarrow \mathrm{H}(-1)\mathrm{N}(0)$$

is detected using a 5:5:1 ratio of gradient areas, since according to Equation 2:

$$5(1.1) + 5(-0.9) + 1(-1.0) = 0 \qquad [3]$$

where the numbers in the parentheses refer to the composite coherence orders. Using these relative gradient areas, protons not coupled with ^{15}N spins may pass through an alternate pathway:

$$\mathrm{H}(+1)\rightarrow \mathrm{H}(+1)\rightarrow \mathrm{H}(+1)\rightarrow \mathrm{H}(-1)\rightarrow \mathrm{H}(-1)$$

which results in a net phase factor:

$$5(1.0) - 5(-1.0) + 1(-1.0) = -1 \qquad [4]$$

Thus, signals from this pathway remain defocused during the acquisition.

A 2D ^{15}N GE-HMQC spectrum of ^{15}N enriched BPTI is shown in *Fig. 2*. The spectrum was collected using a 5 mm inverse probe on an Omega™ PSG 500 spectrometer equipped with an S-17 gradient accessory. Half-sinusoid shaped gradient pulses were applied simultaneously along the X, Y, and Z axes with a maximum gradient strength of ≈20 Gauss/cm and a duration of 3.5 ms. A matrix size of 2048 × 128 resulted in 3.5 Hz resolution in the ω_2 dimension and 10 Hz in the ω_1 dimension. No decoupling was applied.

Gradient-enhanced experiments provide a viable alternative to traditional phase-cycling methods for the selection of coherence pathways. In cases where the sensitivity is adequate, gradient selection can substantially reduce the collection time in multi-dimensional experiments. The ^{15}N GE-HMQC data presented here has none of the t_1-noise from cancellation artifacts usually present in phase-cycled versions of the HMQC experiment. In addition, since the suppression of the single-quantum signals is done prior to acquisition, the receiver gain may be increased, which results in a substantial increase in signal-to-noise. For these reasons, gradient pulses should be the method of choice for coherence selection in HMQC experiments.

Reference

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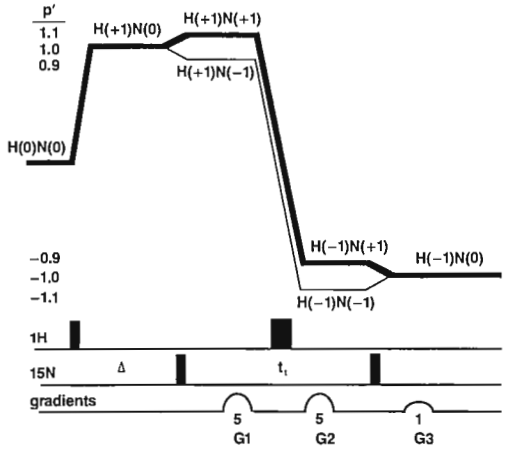

Fig. 1

Pulse Sequence and the coherence pathway diagram for a 15N GE-HMQC experiment.

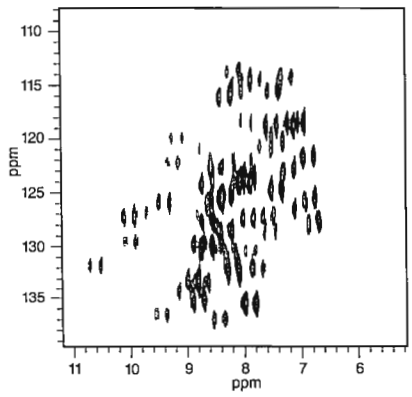

Fig. 2

A 2P Ge-HMQC spectrum of 15N enriched BPTI. The sample was 2.6mM in 90% H2). The data collection time was 2.6 hours.

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Thian C. Ng, Ph.D.
Director, MR Research Center
Division of Radiology / L10
216/444-8209, 216/444-8204

October 16, 1991
(received 10/22/91)

Dr. B. L. Shapiro
Texas A&M Newsletter
966 Elsinore Court
Palo Alto, CA 04303

Dear Barry:

We have recently upgraded our GE CSI 4.7 T/40 cm imaging/spectroscopy system with GE Acustar self-shielded gradient coils (gradient strength up to +/- 20 G/cm). The Acustar minimizes the Eddy current effect and facilitates many fine experiments such as diffusion-weighted imaging which could otherwise not be possible. Now, short TE STEAM and 3D localization/2D phase encoded chemical shift imaging become routine experiments in our laboratory.

Here we report the success of acquiring high spatial resolution of 12 ul (2x2x3 mm) voxel size CSI of cerebral ischemia induced by MCA occlusion in rat brains. Male Sprague-Dawley rats were embolized with silicon cylinder (700 um long x 300 um diameter) (1), mechanically ventilated with 1% halothane, 70% N_2) and 30% O_2. A modified design of ^1H slotted tube resonator (STR) coil (2) of 35 mm diameter was built for this study. To reduce the strong lipid signal from extracranial tissues, 3D localization was used so that Region-Of-Interest (ROI) only included rat brain tissues. The slice offset was chosen according to the diffusion-weighted images. Other parameters were: 3mm slice thickness, field of view (FOV) 64 mm x 64 mm, 32(x) X 32(y) phase encoding steps, voxel size 12 ul (2 mm x 2 mm x 3 mm), TR=1.5 sec, TE-30 msec with 2 averages for each phase-encoding step. Total acquisition time was 51 minutes. 3 Fourier transformations (2D spatial and 1D chemical shift frequency axis) results in spectroscopic images which can be represented as a set of spatially resolved spectra.

To illustrate the quality of the CSI described above. A representative localized ^1H spectrum of one of the multiple voxel acquisitions of living brain and dead brain of a male Sprague-Dawley rat is shown in Fig. 1a and 1b respectively. The main differences between living (Fig 1a) and dead (Fib 1b) brain are as follows: Healthy rat brain does not have lactate (1.31 ppm) and has relatively higher glucose (3.40 and 3.74 ppm) levels compared to dead brain. Others are decreases of NAA, PCr/Cr and Cho, with some increase in glutamate/glutamin (2.2-2.4 ppm) and lipids (.92 and 1.31 ppm) in a dead rat brain. Similar results have also been reported recently by Gyngell et al. (3).

With best regards

Thian C. Ng, Ph.D.

Refs:
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2. A.D. Perez-Trepichio and S.C. Jones. Soc Neurosci Abstr 16, 939 (1990).
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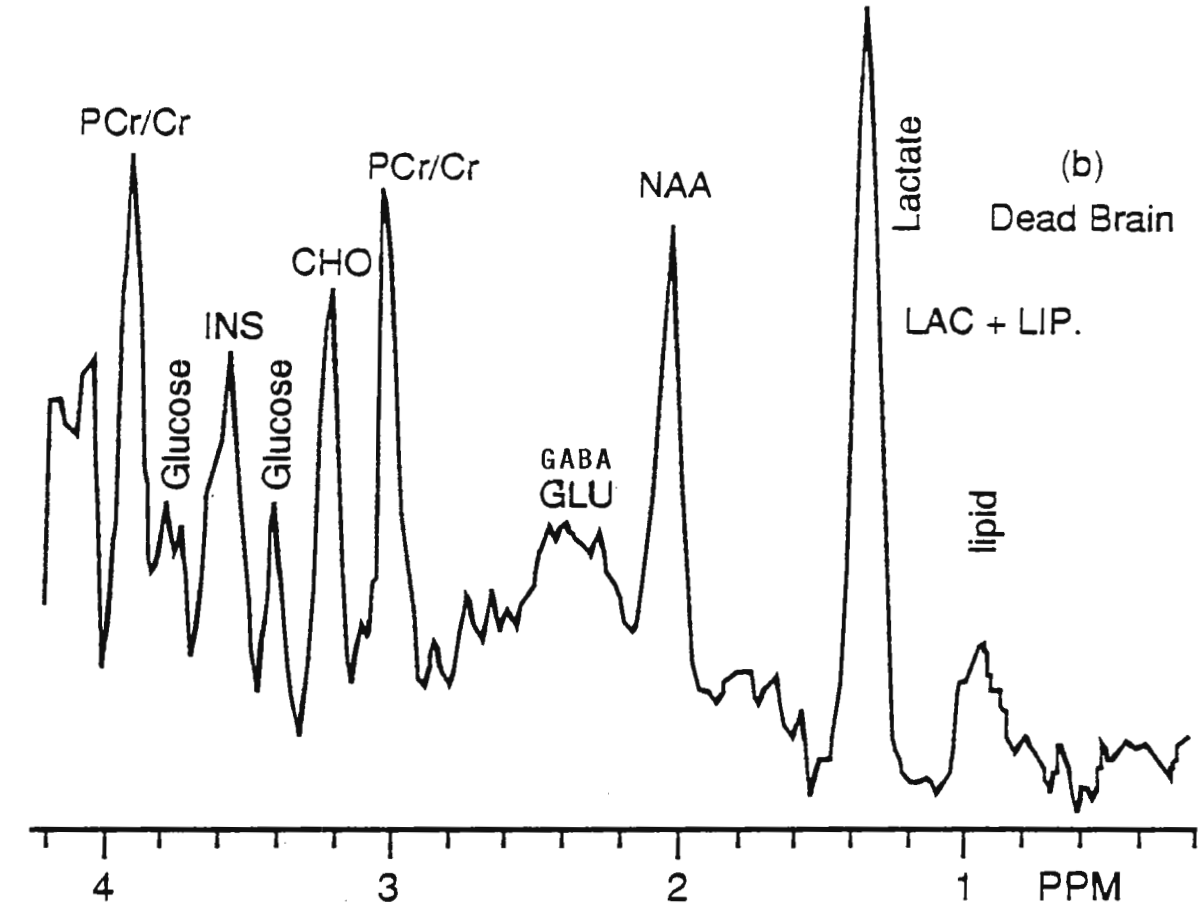
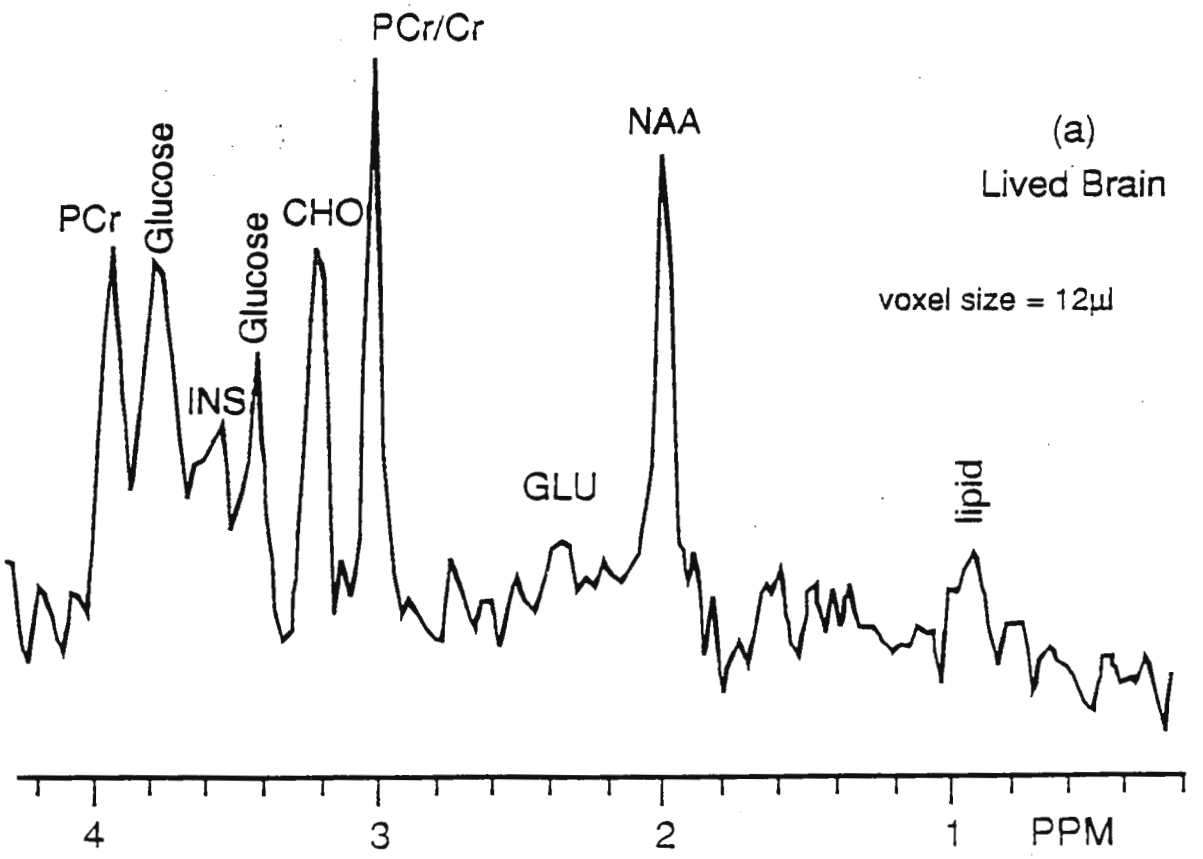

PCr/Cr
Glucose
INS
Glucose
CHO
PCr/Cr
GABA
GLU
NAA
Lactate
LAC + LIP.
lipid
(b)
Dead Brain
4
3
2
1
PPM


PCr/Cr
PCr
Glucose
INS
Glucose
CHO
NAA
GLU
lipid
(a)
Lived Brain
voxel size = 12µl
4
3
2
1
PPM

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DEPARTAMENTO DE QUIMICA

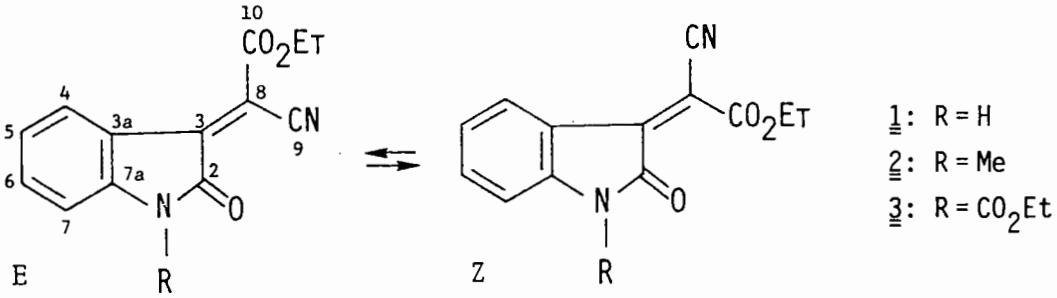
October 11, 1991.
(received 10/30/91)

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

E,Z-Isomerization of Isatylidenecyanoacetates

Dear Professor Shapiro:

As part of an effort to better understand the E,Z-isomerization process of ethyl 2-oxo-3-indolinylidenecyanoacetates[1] (1-3), the effect of the solvent polarity and the presence of traces of acid or base on the dependence of the ^1H NMR lineshapes at room temperature were investigated.



Compounds 1E, 2E, 2Z and 3Z exist as E,Z mixtures in DMSO-d_6. In the case of the 3Z/E mixture, selective broad bands were observed for the H-4 and H-6 E,Z signals and the absorptions owing to 3E are more broadened than those of the 3Z isomer. By addition of traces of HCl fairly sharp lines result (Figure 1). The isomerization of 1E, 2E, 2Z and 3Z followed in pre-acidified DMSO-d_6 shows a deceleration process which was evidenced by the progressive change in the relative populations of the E,Z forms with time. At equilibrium, the E/Z ratio were the same as those obtained in pure DMSO-d_6.

In $CDCl_3$ solutions the nmr spectra of the four studied compounds give fairly sharp lines owing to the corresponding unchanged E or Z forms (Figure 1). Addition of traces of NEt_3 catalyses the geometrical isomerization of all compounds. For 2E or 2Z this process is time depending and a coalescence point is never observed. For 1E and 3Z the equilibrium was established immediately. The fast isomerization of 1E, as compared with its N-Me analogue 2E, may be due to the ionization of the labile N-H bond. In this case, it is possible that the isomerization proceeds *via* the intermediate formation of a mesomeric anion[2].

On the other hand, it is know that the degree of delocalization of the indolinyl nitrogen lone pair by the 2-carbonyl group depends on the electronic influence of the 1-substituent[3]. At this respect it is possible to consider that the E,Z-isomerization could become faster, as the delocalization of the nitrogen lone pair by the carbonyl decreases. This consideration is in accordance with the observed fast isomerization of 3Z, when compared with 2Z, and also in accordance with the

deceleration of the isomerization process when traces of acid are present in DMSO-d_6 solutions. The selective broadening of the nmr lines could be, at least in part, an indication that biradicals are formed[4], considering that these species are very polarizable and can be described appropriately in terms of Pauling resonance by a large contribution from the corresponding zwitterionic structures[5].

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H.M. McConnell and R.E. Robertson, J. Chem. Phys., 29, 1361 (1958).
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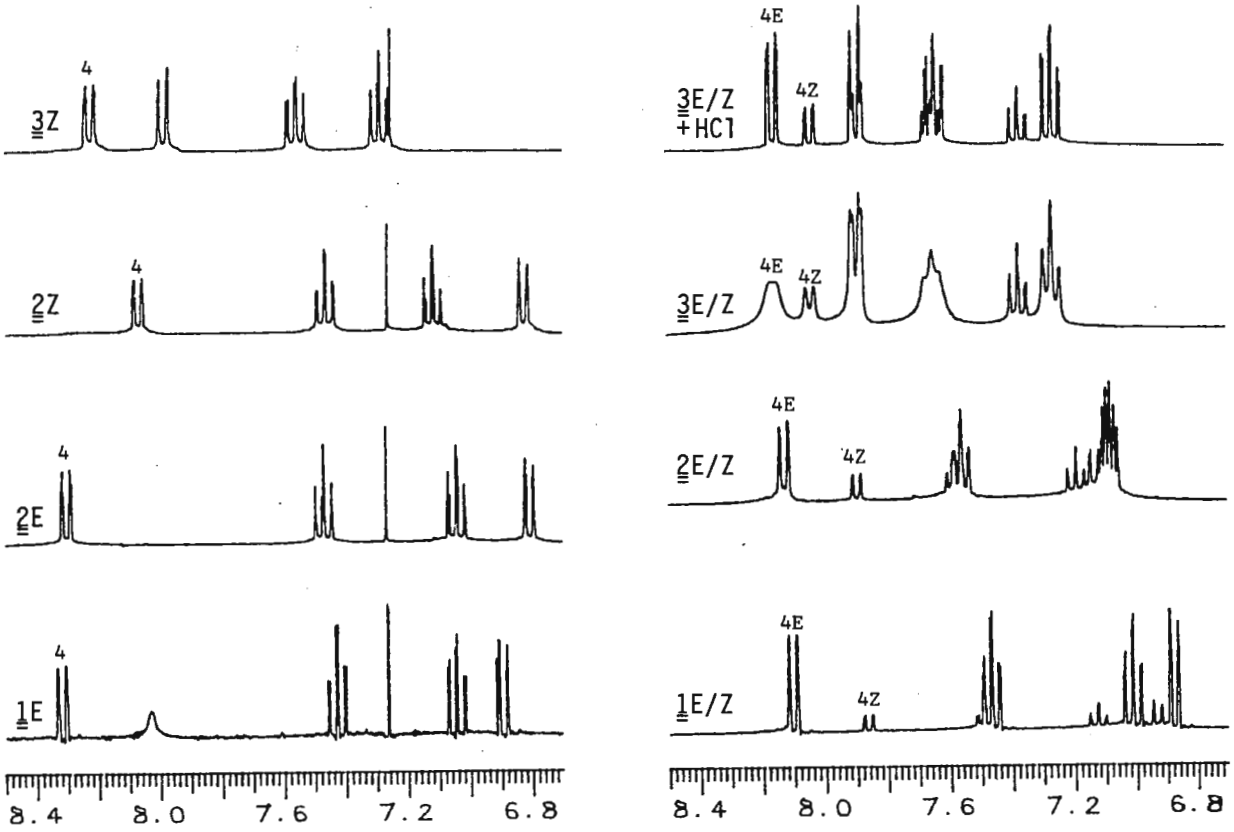

Figure 1. Solvent E/Z-isomerization dependence of isatylidenecyanoacetates. Left in $CDCl_3$; right in DMSO-d_6

Sincerely yours,

Martha S. Morales-Ríos

Pedro Joseph-Nathan

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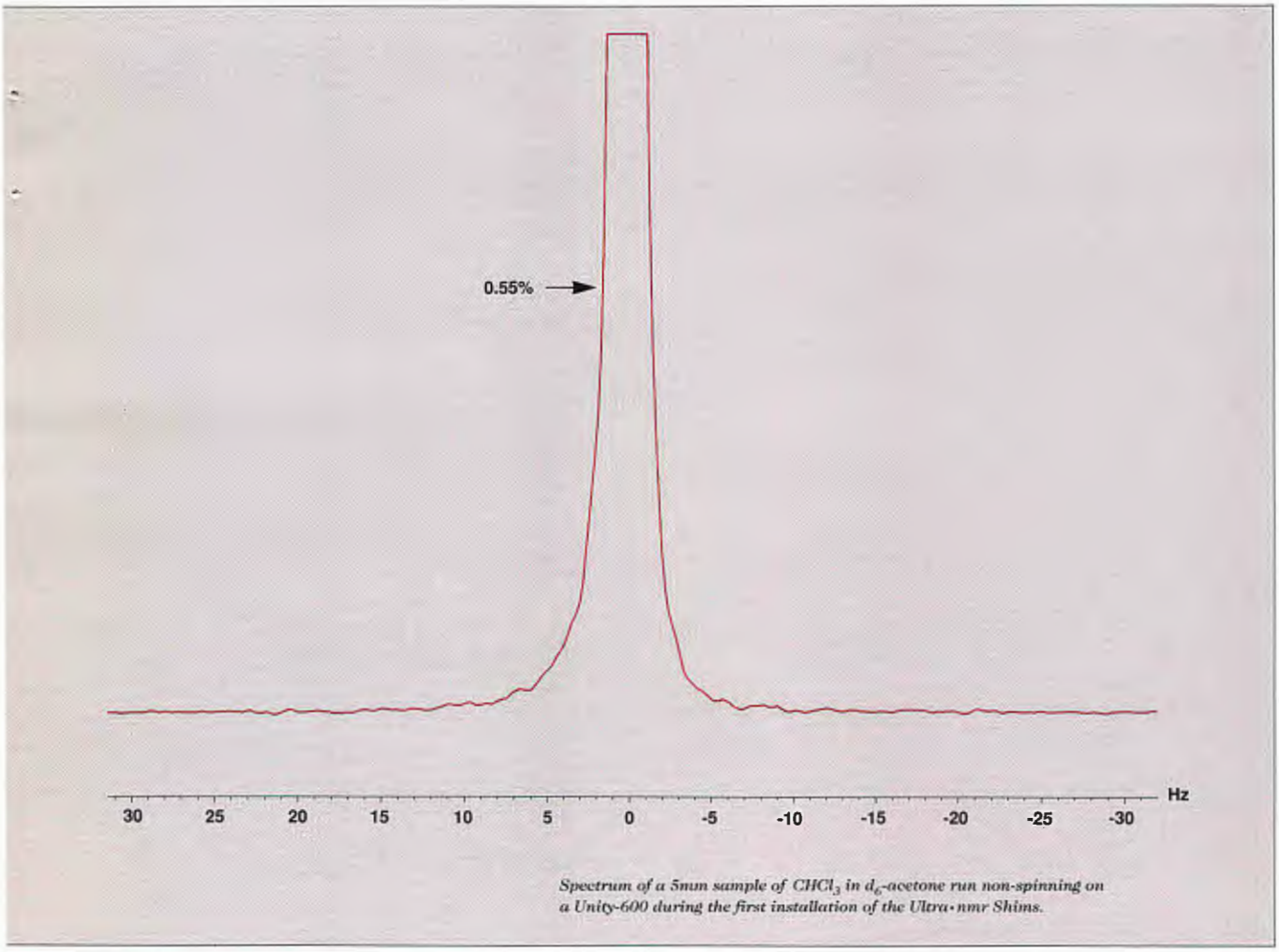

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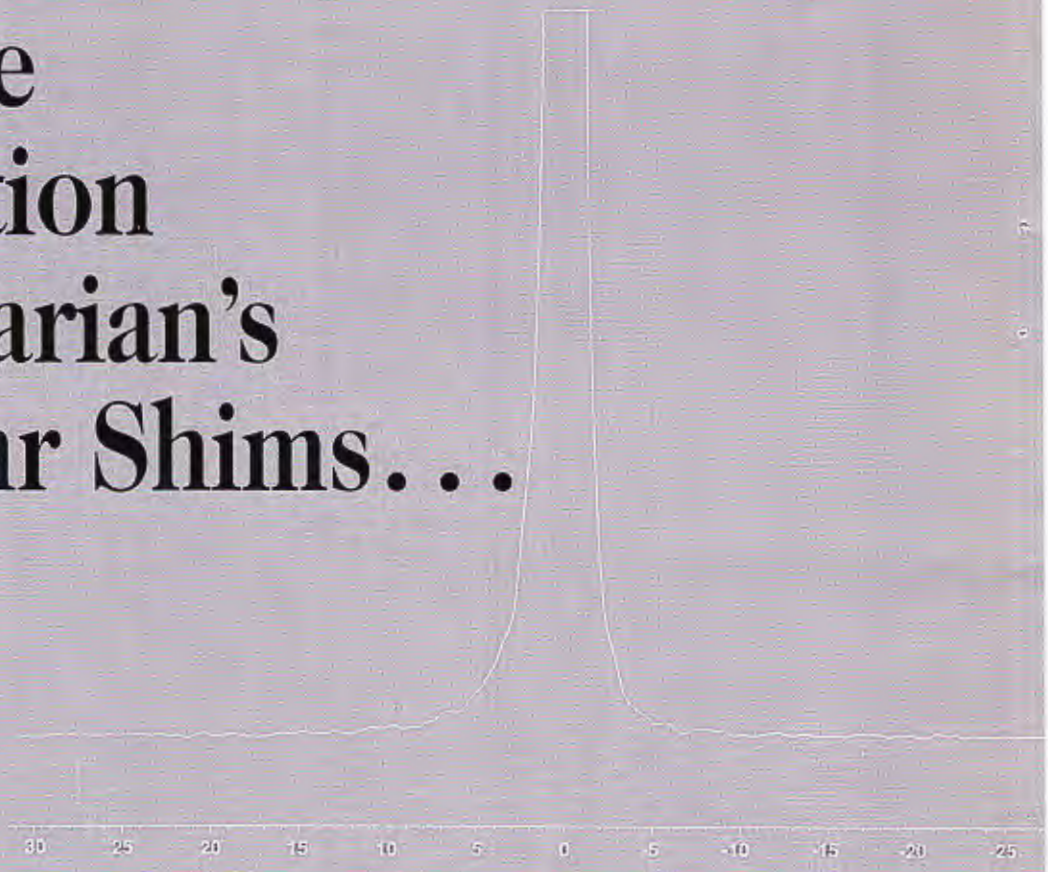

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October 23, 1991
(received 10/28/91)

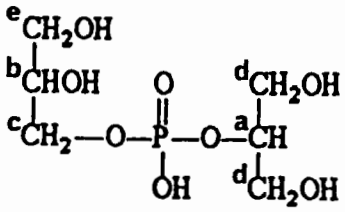
Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Re: Identification of a tumor derived phospholipid headgroup.

Dear Dr. Shapiro:

Recently, Merchant and Glonek described a ^{31}P NMR study of the phospholipid head groups of tumors vs normal tissue.[1,2] They reported the presence of a new resonance at 0.91 ppm, when referenced to glycerolphosphocholine at 0.49 ppm, which appeared to correlate with malignancy. This resonance was independent of pH and did not co-resonate with any known phospholipid head group, suggesting the possibility that a new class of phospholipids had been discovered.

Our laboratory has a history of identifying compounds giving rise to ^{31}P NMR resonances which seem to be metabolically interesting,[3-5] and this one seemed especially intriguing, since differences in ^{31}P NMR spectra of phospholipid metabolism between normal and tumor tissue have often been reported by MRS.[6] We have isolated the compound responsible for this resonance and identified it (by NMR of course) as 2-glycerolphosphoglycerol. (Fig.1,2)



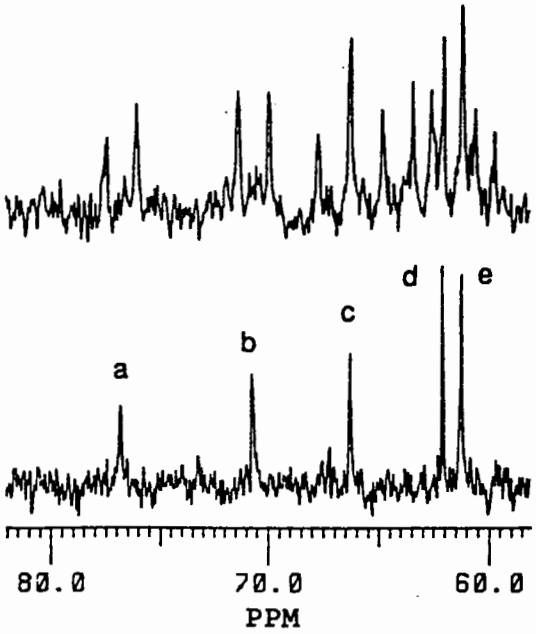


Fig.1. Structure of 2-glycerolphosphoglycerol and it's ^{13}C spectrum run both a) decoupled and b) coupled.

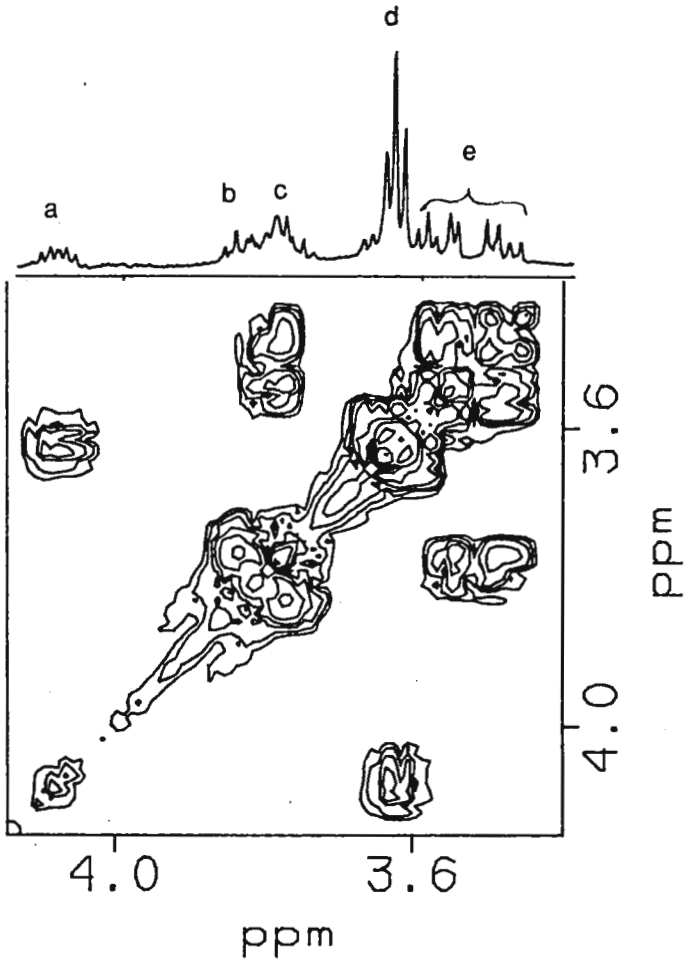


Fig.2. Proton and 2-D COSY of 2-glycerolphosphoglycerol.

Unfortunately, further work on the origin of this interesting phosphodiester demonstrated that it was not the head group of a new class of phospholipids, but rather a complex artifact arising from the isolation procedure employed. However, the consistent increase of this resonance from many tumors suggests that this isolation procedure is measuring some difference between tumors and normal tissue.

Sincerely,

Bangying Su Francis Kappler Benjamin S. Szwergold Truman R. Brown

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Scientific Research Division
Osney Mead, Oxford OX2 0DX, England
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Dr B L Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto
CA 94303
USA

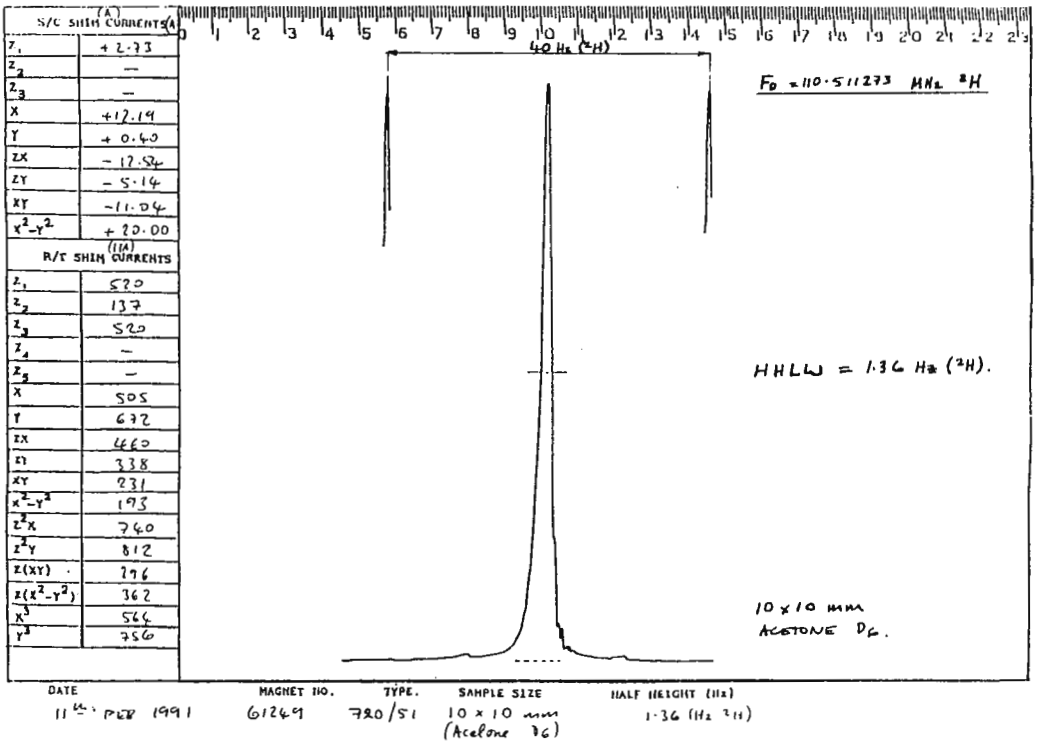
Progress Towards 750 MHz

11 November 1991
(received 11/25/91)

Dear Dr Shapiro

As a result of continued interest and enquiries regarding our 750 MHz magnet development, we feel that it is appropriate at this time to clarify the situation.

Our development has been conducted essentially in two phases. The first involved a significant amount of preliminary work to establish the necessary technologies and culminated in the successful test about one year ago of a 720 MHz prototype NMR magnet system. Before everybody rushes for their order books, it is worth adding a few qualifications to this statement. The magnet achieved its operating field (16.9T) at a temperature of 2.2K. This was achieved by continuous vacuum pumping on the helium bath to enhance the superconductor performance to the necessary level. Field drift and homogeneity were excellent. An early deuterium NMR line from the partially shimmed magnet is shown in the figure shown below. Our field plot results show that true high resolution NMR performance will be achieved using good proton equipment at 720 MHz. This result was announced at the National High Magnetic Field Lab NMR Workshop, Gainsville, Florida on 15 February 1991.



Although this achievement confirmed many aspects of our magnet technology and design criteria, it also highlighted the dangers and difficulties of designing and operating an NMR cryostat at temperatures of 2.2K or below. Since the helium bath is under vacuum at all times, yet it must be topped up from a transport dewar at atmospheric pressure, there is clearly a greater risk of air being sucked into the complicated cryogenic support equipment which could lead to a blockage, pressure build up, magnet quenching or even an explosion. Even with well designed, safety-interlocked cryogenic equipment there can be operational problems: during the three months that the 720 MHz was continuously at field, we had to give it highly skilled attention every three to four days, and the magnet ultimately quenched because of an overnight power interruption which caused the vacuum pumps to stop and the magnet to warm up.

The vibration from the vacuum pumps is a further deterrent to achieving the ultra-stable NMR performance compared with a user-friendly conventional magnet operating unattended at 4.2K, the normal boiling point of liquid helium.

Fortunately you shouldn't have to settle for a pumped system since the second phase of our development, a real 750 MHz operating at 4.2K, is well advanced.

Yours sincerely

Bill Proctor Neil Killoran.

Dr Bill Proctor
Managing Director

Dr Neil Killoran
Technical Manager

In Vivo Magnetic Resonance Spectroscopy V
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This tutorial and workshop will be held just prior to the Experimental Nuclear Magnetic Resonance Conference (ENC) which will be held at Asilomar this year. For an enrollment application, contact Radiology Postgraduate Education, Registration, Room LS-105, University of California, San Francisco, CA 94143-0742 or call (415) 476-5808. Individuals wishing to make presentations should send a brief (1/2 page) abstract to Dr. Gerald B. Matson, DVA Medical Center, MR Unit (11M), 4150 Clement Street, San Francisco, CA 94121

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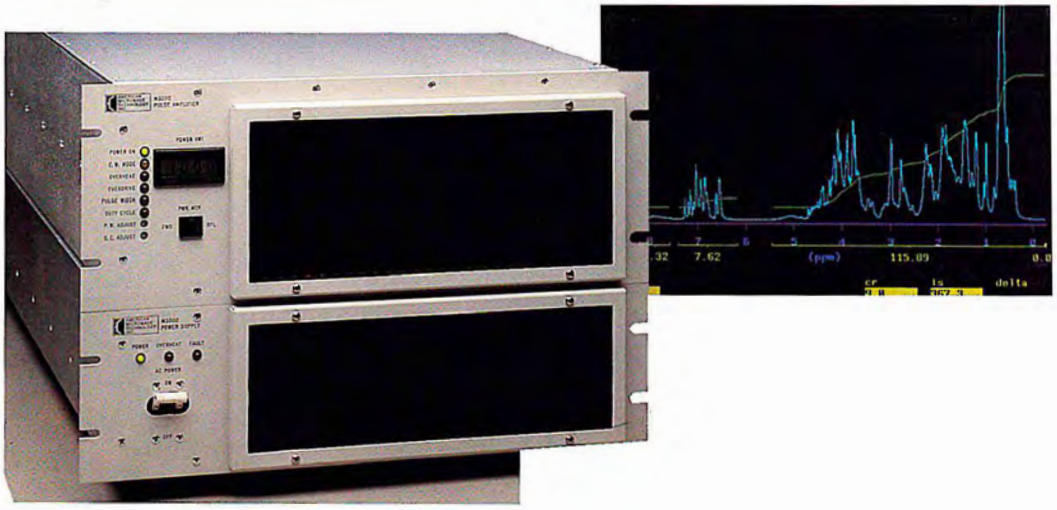

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(to 220MHz)		0-600 W	0-200 W
Gain (typ.)		65 dB	60 dB
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Input VSWR		< 2:1	
Pulse width		20 ms	
Duty cycle		Up to 10%	
Amplitude rise/fall time		200 ns typ.	150 ns typ.
Amplitude droop		5% to 10 ms typ; 7% max	
Phase change/power output		10° to rated power, typ.	
Phase error overpulse		4° to 10 ms duration, typ.	
Noise figure		11 dB typ.	8 dB typ.
Output noise (blanked)		< 20 dB over thermal	
Blanking delay		< 2 μs on/off, TTL signal	
Protection		1. VSWR: infinite VSWR at rated power 2. Input overdrive: up to +10 dBm 3. Over duty cycle/pulse width 4. Over temperature	

Supplemental characteristics:

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System monitors	1. Thermal fault 2. DC power supply fault 3. Over duty cycle/pulse width 4. Forward/Reflected RF power
Front panel controls	1. AC power 2. Pulse width 3. Duty cycle
Cooling	Internal forced air
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Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

October 25, 1991
(received 11/1/91)

Dear Barry:

Long-Range Isotope Effects on ^{13}C Chemical Shifts

You may be interested in some work by Dražen Vikić-Topić, which was begun at the Rudjer Bošković Institute in Zagreb and is now being carried on in our lab.

The effect of isotopic substitution on NMR chemical shifts has been studied for many years. In general, the "direct" zero-bond isotope shift has been found to be negligible, whereas "indirect" effects through one or more bonds are often quite significant. Most of the rather extensive theoretical treatments have dealt with one-bond effects -- that is, the change in chemical shift of a nucleus when an isotopic substitution is made in an immediately bonded atom. As expected, the largest isotope effects are found when ^{2}H is substituted for ^{1}H, but they are observed most readily in the chemical shifts of nuclei with large chemical shift ranges, such as ^{13}C and ^{19}F.

Isotope effects are often measured in systems where the isotopically substituted atom is removed from the nucleus whose chemical shift is observed by more than one bond. As higher magnetic field instruments have become available, small but measureable isotope effects have been observed for nuclei that are quite remote from the site of substitution. For example, the data given in the accompanying Table come from a number of para-deuterated or para-fluorinated extended aromatic compounds, consisting of two benzene rings linked with different unsaturated groups. With 400 or 500 MHz spectrometers, deuterium isotope effects as large as 3 or 4 ppb are observed on the chemical shifts of carbons 10 bonds away from the site of substitution. [Since the samples contain both normal and isotopically substituted molecules, differences of this magnitude (~0.4 Hz) are readily measured.] As shown in the Table, there is a rough correlation between the magnitudes of the isotope effects and long-range C-F couplings for molecules in which fluorine has been substituted for deuterium. We anticipate that this correlation will help us understand the mechanism responsible for transmission of the isotope information through the long conjugated system.

Please note that we followed your guidelines for margins and have given you a lot of blank space below. Sorry, but the Table has to go on the next page.

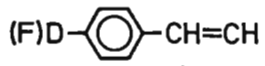
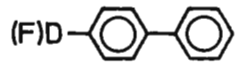
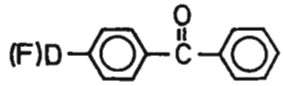
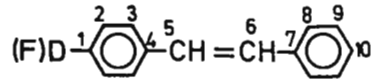
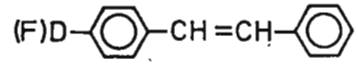
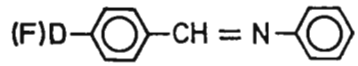
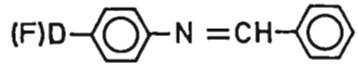
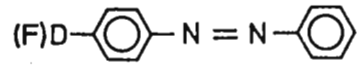
Sincerely,

Dražen Vikić-Topić

Edwin D. Becker

Vikić-Topić, Becker

Long-Range Deuterium Isotope Effects ($^nΔ$/ppb)[a] and Long-Range Carbon-Fluorine Coupling Constants ($^nJ_{CF}$/Hz)[b]

Molecule		C-atom (n)	5	6	7	8	9	10
1		Δ	-8	12				
		J	0.59	2.34				
2		Δ	-10	0	0	4		
		J	0	0.60	0	0.27		
3		Δ	-5	-4	0	0	0	
		J	0	0	0	0	0	
4	 (t)	Δ	-9	10	-2.8	0	0	2.8
		J	0.98	2.43	0.70	0.35	0	0.28
5	 (c)	Δ	-9.5	8.7	-2.4	0	0	2
		J	0.21	1.21	0	0	0	0
6	 (t)	Δ	-6.5	N	-2.9	0	0	0
		J	0.98		0.48	0.24	0	0
7	 (t)	Δ	N	6.9	0	0	0	0
		J		1.63	0.33	0	0	0
8	 (t)	Δ	N	N	-6.8	0	0	3.6
		J			0.70	0	0	0.28

a) A positive sign indicates that the carbon is more shielded in the deuterium-substituted molecule. **n** denotes the number of intervening bonds between interacting nuclei. Digital resolution: 0.25 ppb. Acetone-d_6 solutions.

b) In $CDCl_3$ solution. Digital resolution: 0.03 Hz. ↓ **More blank space!** ↓

ROCKY MOUNTAIN CONFERENCE

34th ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

The 34rd Rocky Mountain Conference on Analytical Chemistry will be held August 2nd through August 6th, 1992, at the Denver Radisson Hotel in Denver, Colorado.

The 1992 program will include symposia on:

- Atomic Spectroscopy
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- Computer Applications, Robotics and Chemometrics
- Electron Paramagnetic Resonance
- Electrochemistry
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- Hazardous Waste
- ICP/MS
- Laboratory Total Quality Management
- Luminescence
- Mass Spectrometry
- Near IR Spectroscopy
- Nuclear Magnetic Resonance
- Pharmaceutical Analysis
- Robotics
- Quality Assurance

Further information on individual symposia is available from the individual program chairs, or the Conference Publicity Chair, Patricia Sulik, Rocky Mountain Instrumental Laboratories, 456 S. Link Lane, Ft. Collins, CO 80524 (303) 530-1169.

During the Conference, the Colorado Section of the American Chemical Society is will sponsor several short courses. Further information on ACS Short Courses will be available later.

Additional Seminars, User's Group Meetings, including the Bruker User's Group, and courses will be offered.

An Exhibition of analytical instrumentation, supplies and services is held in conjunction with the Conference. To reserve exhibit space, contact Jim Parker, Manville Tech Center, Mail Stop R-38, P.O.Box 5108, Denver, CO 80217, phone (303) 978-5481.

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Ft. Collins, CO 80523
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Chemistry Department
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24.10.1991
(received 11/1/91)

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

Signal narrowing for paramagnetic molecules

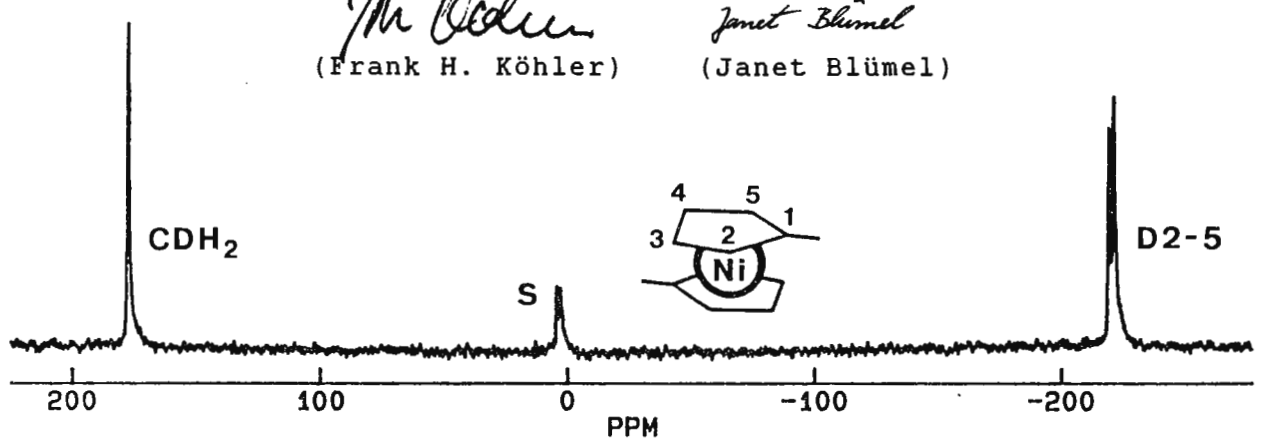
Dear Dr. Shapiro,
one of the reasons why this letter is a bit late was the replacement of our old CXP 200 by a MSL 300 machine early this spring. I should rather say it <u>is</u> the reason because the projects that we would have loved to communicate still cannot be done. An annoying number of hardware (notably probehead) problems frustrated our effort and some of these problems have still to be cured.

For all that, we could do an experiment which aimed at the improved resolution of the NMR spectra of paramagnetic organometallics. A nice example is 1,1'-dimethylnickelocene shown below. Theory says that owing to its (quasi) $^2E_{1g}$ ground state the electron spin density at C2/5 and C3/4 should be almost equal. In fact, we obtained only one NMR signal for H2-5 with our CXP machine although the symmetry requires two. Can they be resolved?

We have shown earlier (J. Magn. Reson. 27(1989)798) for some very simple paramagnetic metallocenes that on passing from ^1H to ^2H NMR the signal half width decreases by a factor of up to 42. The method is not particularly cheap because one has to synthesize ^2H-enriched compounds in order to overcome the inherent low receptivity of ^2H NMR and the fact that paramagnetic ^2H signals may be still large. We have now succeeded in recording the natural abundance paramagnetic ^2H NMR spectra of some 1,1'-dimethylated metallocenes. The result shown below for the nickel derivative is very satisfying and the answer to our earlier question is: yes, D2-5 do give two signals which are separated by only 1.84 ppm at 55 °C.

With best regards

(Frank H. Köhler) (Janet Blümel)



399-36

Washington
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Department of Chemistry

October 16, 1991
(received 10/19/91)

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

Dear Barry:

I wish to submit for publication in the *Texas A&M University NMR Newsletter* the following Symposium announcement.

The Sixth Washington University-ENI/Emerson Electric Company Symposium on Nuclear Magnetic Resonance will be held Monday, May 18, 1992, in the Department of Chemistry at Washington University in St. Louis, Missouri. The symposium will feature: **Richard Ernst**, Laboratorium für Physikalische Chemie Eidgenössische Technische Hoschschule; **Juli Feigon**, University of California at Los Angeles; **Robert Griffin**, Massachusetts Institute of Technology; **Harden McConnell**, Stanford University and **Hans Thomann**, Exxon Research and Engineering Company. The symposium, sponsored by Emerson Electric Company, is open to all interested in the development and application of new techniques in nuclear magnetic resonance. For additional information, contact symposium coordinator Karen Klein at (314) 935-6405.

Thank you for your help in placing this announcement.

Sincerely yours,

Jake

Jacob Schaefer
Professor of Chemistry

JS/kk

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Prof. B. L. SHAPIRO
Editor
TAMU NMR Newsletter
966 Elsinor Court
Palo Alto, CA 94303

U. S. A.

N./Réf.
V./Réf.

Wissembourg, le 30 octobre 1991
(received 11/16/91)

Dear Barry,

Is is well known by spectroscopists that the "inverse experiment"[1] is now the technique of choice to observe low γ and/or low abundance nuclei when those are coupled to high sensitive ones. The advantage of the "inverse" experiment is the large gain in sensitivity, and therefore in experimental time, provided by the observation of the nucleus with the highest γ. Where the sensitivity is increased by a factor γ_H / γ_X between an observation of the X nucleus in the "direct mode" and its observation after an INEPT transfer, it is increased by a factor $(\gamma_H / \gamma_X)^{5/2}$ when using an inverse experiment. When for example one wants to observe ^{183}W, the gain of the inverse observation through a ^{31}P - ^{183}W correlation is in the order of 295 compared to the direct observation of ^{183}W and in the order of 30 compared to the observation of ^{183}W after an INEPT transfer. This technique has been widely applied over the past ten years, using ^{1}H, ^{31}P or ^{19}F to observe various kinds of low γ nuclei[2].

In the course of our investigations, we had to determine the different connectivities between ^{31}P and ^{183}W and the values of the homonuclear ^{183}W-^{183}W coupling constants for the following polyoxoanion $[P_6W_{18}O_{79}]^{20-}$. We decided to use the "Overbodenhausen" pulse sequence[3], and could observe in one experiment, the different heteronuclear connexions as well as the homonuclear ^{183}W-^{183}W coupling constants.

The experiment was run on an AMX300 equipped with triple resonance, and an inverse probe with the observe channel tuned on ^{31}P , and the decoupling coil tuned on ^{183}W. The 2D map represented in Fig. 1 shows the different ^{31}P - ^{183}W connectivities. Fig. 2 represents the column corresponding to the ^{31}P at - 5.5ppm from which one can directly read the homonuclear ^{183}W-^{183}W coupling constants by inspecting the satellites of the ^{31}P - ^{183}W central peaks.

Best wishes.

Dr C. BREVARD

A. BELGUISE

Dr R. THOUVENOT
Univ. Paris VI

1: Maudsley A. A., Ernst R. R., Chem. Phys. Lett. (1977) 50, 368.
2: a) Benn R., Brevard C., J. Am. Chem. Soc. (1986) 108, 5622
b) Bourdonneau M., Brevard C. Inorg. Chem (1990) 29, 3270
3: Bodenhausen G., Ruben B. , Chem. Phys. Lett. (1980) 69, 185

Fig. 1: 2D inverse 31P–183W correlation, amx300

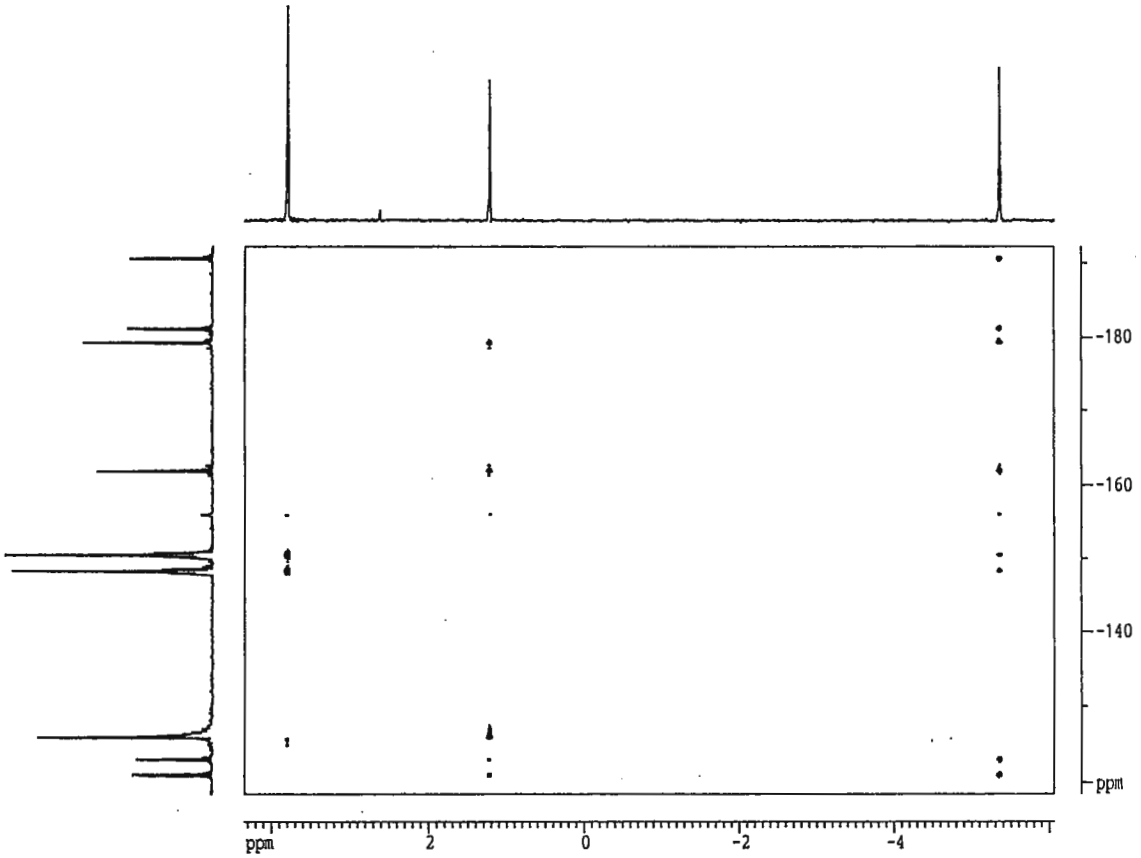
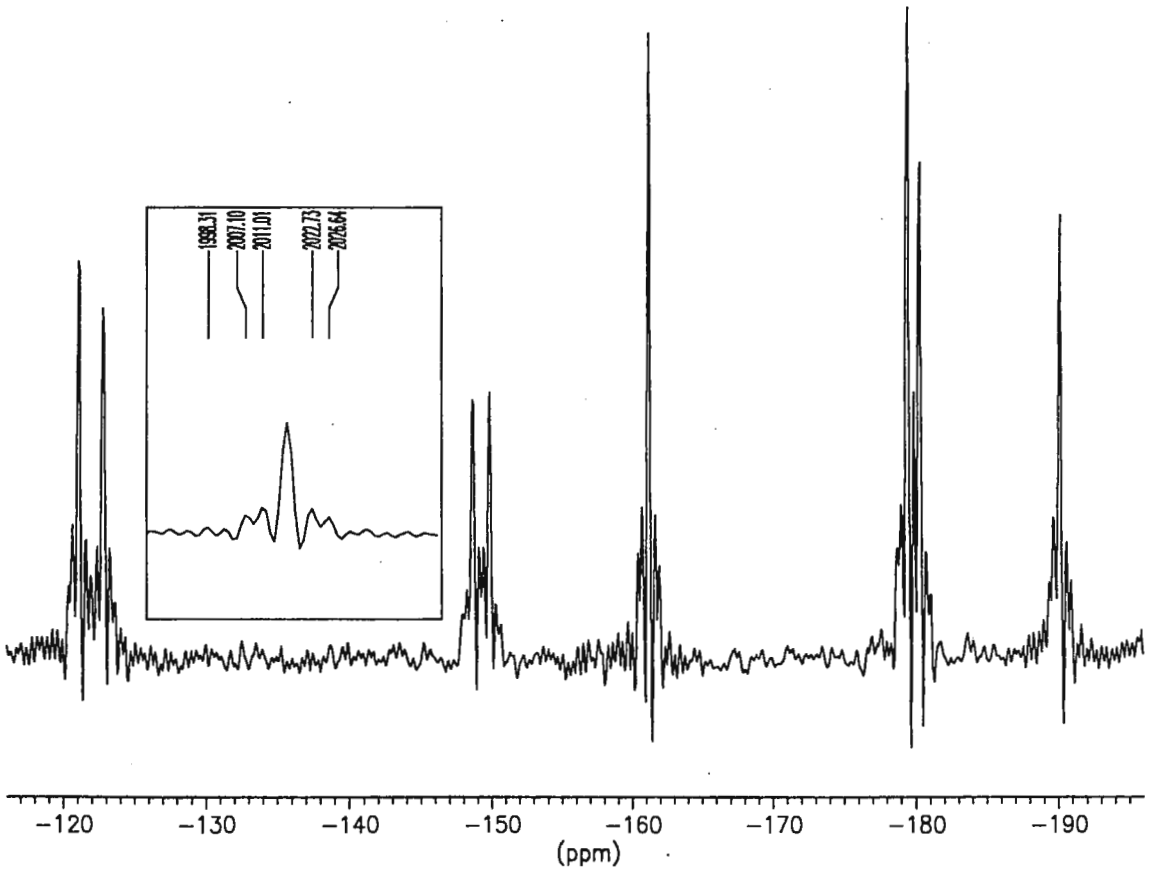


Fig. 2: Column of the inverse 2D experiment 31P–183W corresponding to the 31P at –5.5ppm. The homonuclear coupling constants 183W–183W can be obtained by inspecting the satellites of the central peaks.



UXNMR* and WINNMR.*

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. Our software for personal computers (WINNMR) is based on MS-Windows* for 80X86 computers, and on Mac*OS for Macintosh* IIs. WINNMR allows NMR processing with convenient access to all your favorite PC and Mac software packages. To see how you can enhance your NMR networking, simply ask for more information about our NMR software.

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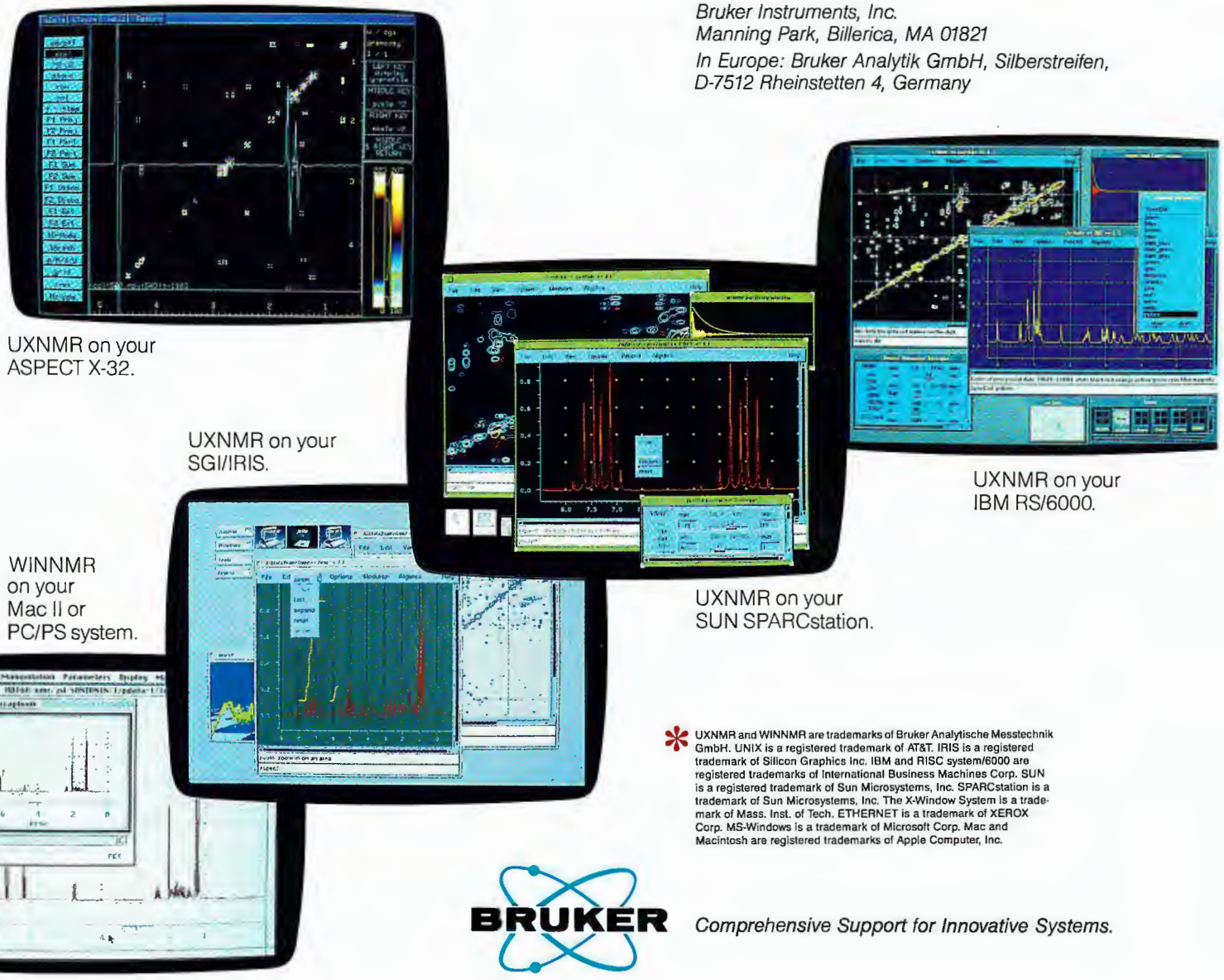

UXNMR on your ASPECT X-32.

UXNMR on your SGI/IRIS.

UXNMR on your IBM RS/6000.

WINNMR on your Mac II or PC/PS system.

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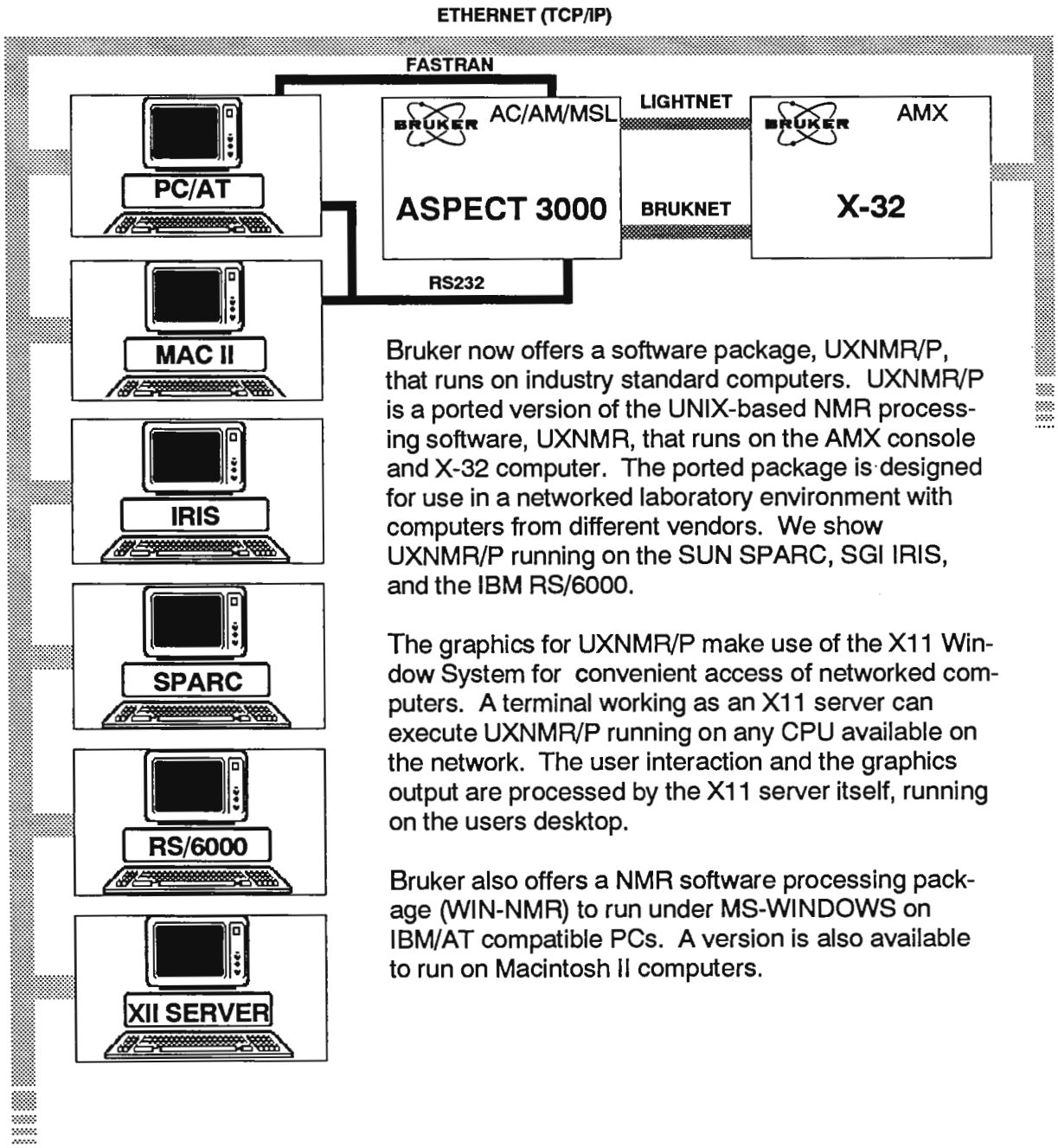

Bruker now offers a software package, UXNMR/P, that runs on industry standard computers. UXNMR/P is a ported version of the UNIX-based NMR processing software, UXNMR, that runs on the AMX console and X-32 computer. The ported package is designed for use in a networked laboratory environment with computers 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

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

October 25, 1991
(received 11/2/91)

Re : Extent of ^{15}N Labelling of the fungal peptide alamethicin: Spin Echo Difference Spectroscopy

Dear Dr. Shapiro,

We have isotopically labelled the 20 amino acid peptide alamethicin with ^{15}N by growing the fungus *T. viride* in a modified basal medium. We used dextrin as the carbon source instead of the published carboxymethyl cellulose[1] and $K^{15}NO_3$ as the sole nitrogen source. From the small, broad ^{14}N-bound amide peaks in the ^{1}H NMR spectrum of alamethicin (Figure 1), it is evident that labelling is not 100%. Since the NH resonances of each amino acid, except for valine 15 and phenylalaninol 20, are well resolved, it was possible for us to use 1-D Spin Echo Difference Spectroscopy[2] to determine the extent of labelling at each site. Figure 2 shows the normal spin echo ^{15}N-decoupled spectrum acquired on a Bruker AMX500. Figure 3 shows the spectrum with the same pulse sequence except that a 180° pulse was applied to ^{15}N. Figure 4 is the sum of Figures 2 and 3 while Figure 5 is the difference of Figures 2 and 3. By measuring the ratios of the peak integrals of the sum to the difference spectra, we were able to determine the extent of ^{15}N labelling which ranges from 85% to 92% with the highest labelling at the glutamine sidechain amides. We are now attempting a uniform ^{13}C labelling.

Please credit this contribution to the account of Ted Schaefer in our department.

Sincerely,

A.A. Yee

Joe O'Neil

[1]Brewer,D., Mason, F.G., & Taylor,A (1987) *Canadian Journal of Microbiology 33*, 619-625.
[2]Griffey, R.H., Redfield, A.G., Loomis, R.E., & Dahlquist, F.W. (1985) *Biochemistry 24*, 817-822.

Acetyl-B-P-B-A-B-A-Q-B-V-B-G-L-B-P-V-B-B-Q-Q-O
where B is α-aminoisobutyric acid
O is phenylalaninol

Figure 1:

Figure 2:

Figure 3:

Figure 4:

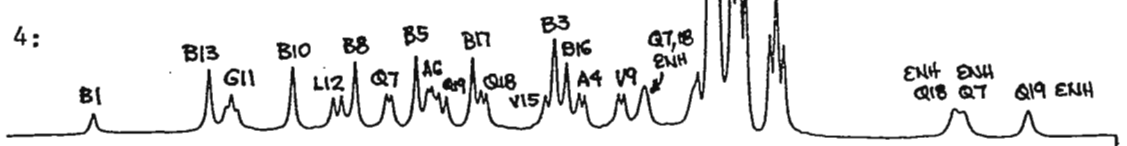
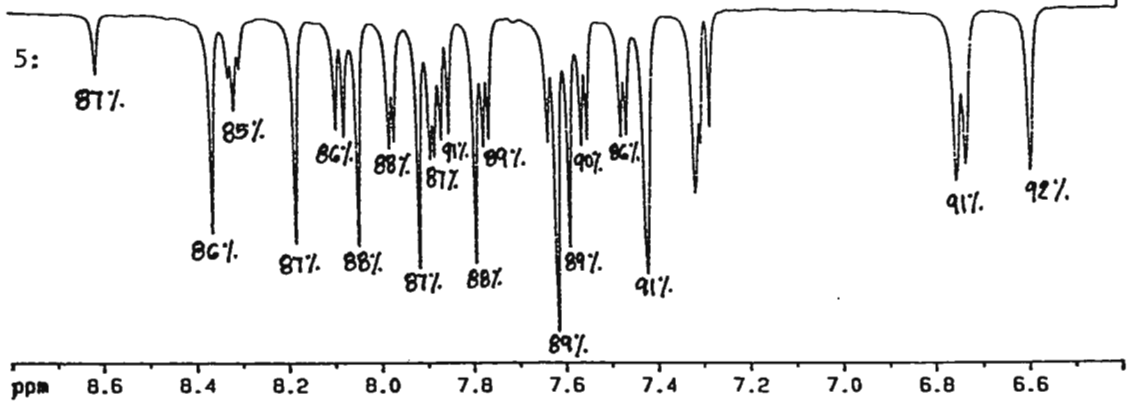


Figure 5:



UNIVERSITY OF ST. ANDREWS

From: Dr. F. G. Riddell

DEPARTMENT OF CHEMISTRY,
THE PURDIE BUILDING,
THE UNIVERSITY,
ST. ANDREWS,
FIFE KY16 9ST
SCOTLAND

Tel: (0334) 76161 Ext. 8364
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25th October 1991
(received 10/31/91)

Professor B.L. Shapiro
966 Elsinore Court
Palo Alto
California 94303

Dear Barry,

Tetraisopropylethylene in the solid state

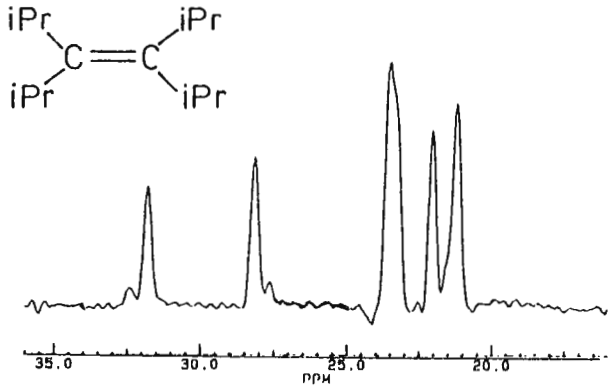
It was a pleasure to meet you and so many old friends again in St Andrews this summer for the Royal Society of Chemistry nmr meeting. However, such pleasures pale into insignificance when one receives the dreaded **ultimatum**!

One of the great things about our new MSL 500 is the excellent resolution obtainable for ^{13}C spectra of solids. We generally obtain a line width on the CH_2 of adamantane of 4.5Hz which is better than the 6Hz specification. When this is added to the large dispersion available it means that we can resolve lines in ^{13}C CPMAS spectra that would be difficult to separate on lower field spectrometers.

One compound we looked at recently bears this out - tetraisopropylethylene, kindly given to us by Edgar Anderson. The interest in this compound is that isopropyl group rotation is frozen out in solution at room temperature. The crystal structure was solved by Simonetta's group, (Tet. Letts, 1980, **21**, 2345-2348). The space group is $P\bar{1}$ and they found 15% of the molecules occupying disordered positions. The space group indicates that there should be 4 non-equivalent methyls and 2-non equivalent methines in the asymmetric unit of the solid.

These can be seen allowing for a methyl shoulder in the aliphatic region of the moderately resolution enhanced CPMAS spectrum of the aliphatic region at 203K. In addition each methine has a satellite line of the correct intensity arising from the disorder.

It is very nice when solid state nmr agrees with X-ray crystallography. When it doesn't I know which technique I believe in, as bitter experience has taught me that crystallographers can, and sometimes do, get it wrong!



Best wishes,

Yours sincerely,

Dr F G Riddell

399-44

DEPARTMENT OF HEALTH & HUMAN SERVICES — Public Health Service

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Bethesda, Maryland 20892
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(301) 496- 8140

Date: 11/14/91 (received 11/15/91)

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

How many spin echoes can one get from two RF pulses?

Dear Dr. Shapiro,

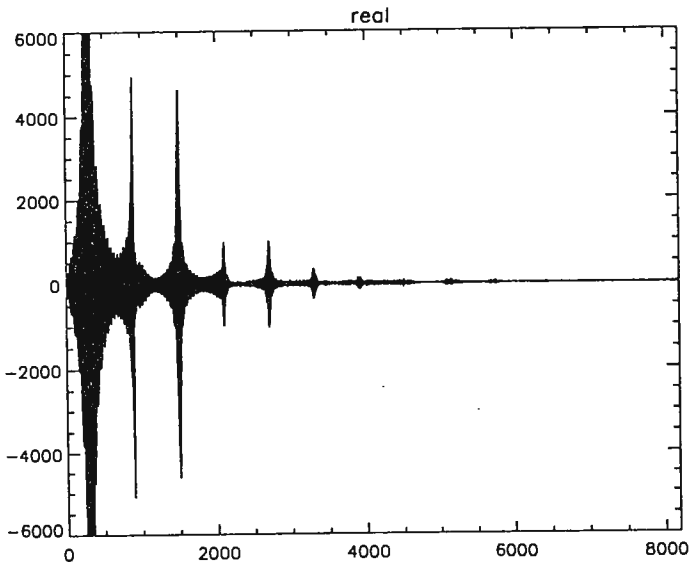
Recently, while checking out our 4.7T/40 cm bore GE CSI instrument with a simple $\pi/2 - \tau - \pi$ -acq pulse sequence on a fairly large phantom in a 10 cm birdcage coil, we heard from the speaker receive-output a noticeable "ringing". We looked a little closer at this surprising phenomenon . A particular receive output is given in the Figure. As you can see, many many spin echoes.

At first a bit puzzled, we realized that this (again, unfortunately) is nothing new. It is caused by radiation damping. This gives an additional term in the Bloch equations of the form $(\partial M/\partial t)xM$. The figure shows a particularly nice example of a series of harmonics. For a recent, detailed paper on radiation damping see W.S. Warren, S.L. Hammes, J.L. Bates, J. Chem. Phys. 91, 5895-5904, 1989.

So, what can we do with it? Apart from keeping our subscription going, not very much at first sight. For us imagers, it is nice that with minimal RF power a lot of echoes can be generated. Maybe, a new ultra-fast imaging method can be designed. Unfortunately, as soon as you switch on a field gradient, radiation damping is gone.

Sincerely Yours,

Peter van Gelderen Chrit Moonen



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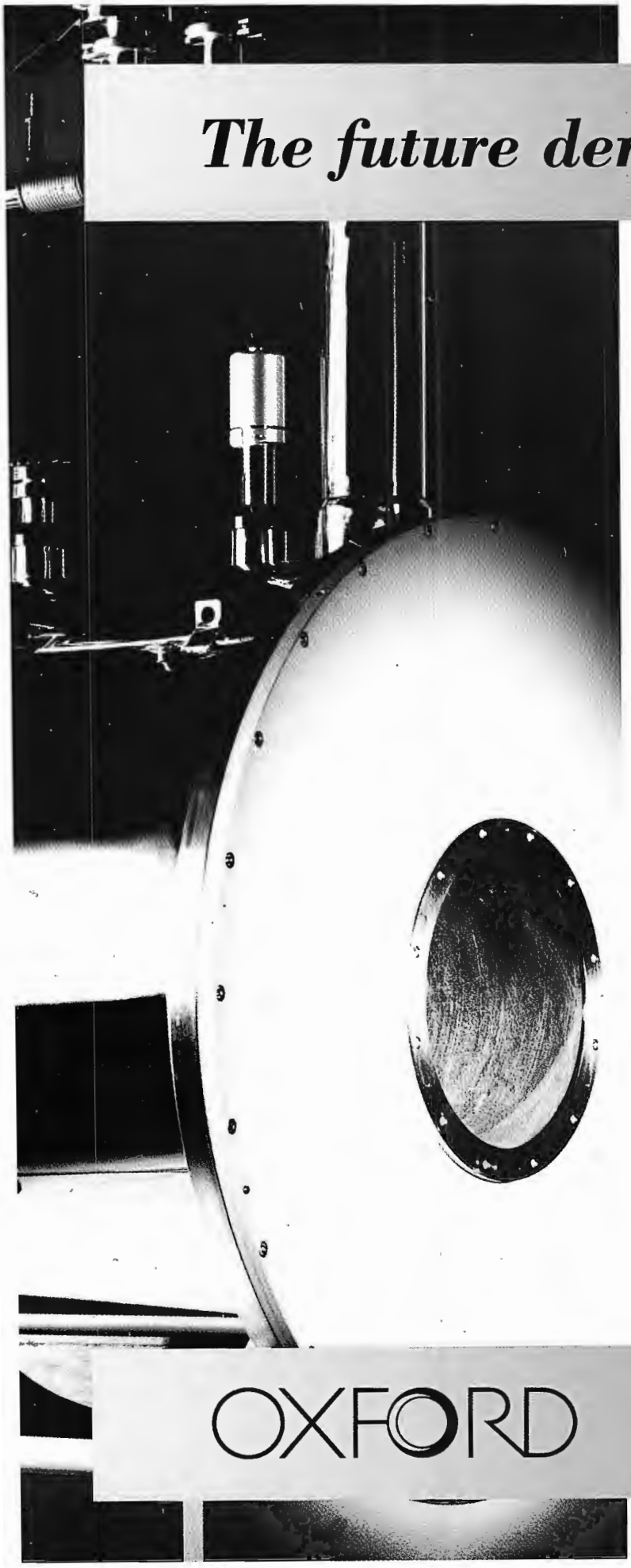

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October 3, 1991
(received 10/15/91)

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

Interfacing of ASPECT 3000 to Sun SPARCstation 2 Without On-site Ethernet

Dear Dr. Shapiro,

We recently acquired a Sun SPARCstation 2 equipped with a 1.2 Gbyte external hard drive and 1.3 Gbyte 4 mm DAT drive (Ardat). The SPARCstation will function primarily as a workstation for our Bruker AM 300 NMR spectrometer. Interfacing our Bruker ASPECT 3000 to the Sun SPARCstation 2 and getting the two systems to communicate with each other was not as easy as we expected. The difficulties we encountered involved hardware and software concerns on both systems.

Linking Bruker's Ethernet communications box with the ASPECT 3000 disk interface board and the corresponding disk drive was straightforward. However, because we will not have on-site Ethernet available for at least another year, some modifications had to be made in linkng the Ethernet communications box to the SPARCstation. Using a thick Ethernet cable, we connected the communications box to a transceiver containing a BNC tap (Cabletron's ST-500 Ethernet and IEEE 802.3 transceiver with LANVIEW). At the BNC tap of the transceiver, we put a BNC "T" connector, to which we connected a 50 ohm load and a 50 ohm BNC cable. The other end of the 50 ohm BNC cable is connected to another transceiver, also with a BNC "T" connector and a 50 ohm load. A thick Ethernet cable then links this second transceiver to the Ethernet port on the SPARCstation.

Although the hardware was assembled, we encountered problems due to a bad chip on one of the boards in the communications box. We also discovered that we needed to upgrade the ASPECT 3000 disk interface board from ECL04 to ECL08. This upgraded disk interface board can considerably slow down the disk I/O. On the SPARCstation, we had to modify the configuration to handle Ethernet. We also had to check that we had installed the latest matching versions of Bruker's communications software on both systems. After these further modifications, we are now able to transfer data files between the ASPECT 3000 and the SPARCstation.

Currently, we are evaluating NMR processing software for the SPARCstation. The ease and accuracy of plotting spectra is included in our evaluation. Our HP LaserJet II laser printer is connected in parallel with the SPARCstation which is using NeWSprint software to handle the Postscript processing, which is required by the NMR processing software. The laser printer, which is equipped with 4 Mbytes of memory and an HPGL cartridge (Data Pacific), is also connected in series with the ASPECT 3000. To handle interactive plots, we have disengaged the auto-eject feature on the laser printer and use the command NP (New Page) on the ASPECT 3000 to form feed plots.

In the future, we will be evaluating data archiving software on the SPARCstation as well as the networking of the SPARCstation to MAC's, PC's, and to a proposed 500 MHz NMR spectrometer.

Ka-Pi Hoh

Kurt F. Wollenberg

G. Paul Sutton

Dr. Bernard Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 940330, U.S.A.

October 10, Turku, 1991
(received 10/24/91)

PROTON NMR AS A RAPID METHOD FOR DIAGNOSIS OF METABOLIC DISORDERS

Several genetic disorders of metabolism cause accumulation of metabolic intermediates in the body. These intermediates also secrete into urine. The increased concentration of these intermediates in urine can in turn be used as basis for diagnosis. Often when the metabolism of aminoacids is disturbed the intermediates are organic acids as in case of lethal TYROSINEMIA (lack of fumarylacetoacetate EC 3.7.1.2.)

When this kind of disease is suspected, and especially when the patient is new-born, child, a rapid method for diagnosis is needed. Normally the analysis would be based on HPLC method, but the method needs preparation of the sample which may be tedious and time consuming. That is why it was decided to test whether ^1H NMR could be used as an analytical tool in this respect. The idea was to run NMR spectrum directly from untreated urine to identify the organic acids possibly present. The spectrum is, of course, very complicated due to the nature of the sample. However, it should be possible to realise if a certain metabolite is present at a higher than normal concentration. This was indeed the case.

The samples were prepared from urine by filtrating it and adding 10% of D_2O to enable field locking. Urine consists mainly of water and in practise the concentration of water is 55 mol/l. On the other hand the metabolites searched for were present in a mmol scale. This meant that the water signal had to be supressed. There is several methods for doing this but we found that a simple gated decoupling gave the best results. Of course, some information near to the water signal is lost. However, the metabolites which we were searching for gave signals also in the undisturbed regions.

To identify the metabolites wanted, standard spectra were run for model compounds by adding them to the urine of a normal person. Since the metabolites were mainly acids, the pH and hence also the chemical shifts of the model compounds depend on the concentrations. To overcome this problem the standard samples were prepared in three dilutions. By comparing a patient sample with the standards it was often fairly easy to identify contaminants due to metabolic disorders. Accurate quantification was, however, difficult. Fortunately secretion of creatinine into urine is constant and hence it could be used as an internal standard. In many cases the method appears to be accurate enough to enable a proper diagnosis to be made and to help to select a necessary therapy.

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Department of Physiology and Biophysics

October 14, 1991
(received 10/18/91)

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

Dear Barry,

Double Quantum Filtered ^{23}Na NMR of Perfused Rat Heart

We have previously shown that there is a significant contribution from extracellular Na^+ to the detected double-quantum filtered (DQF) signal in red blood cells and in the rat heart perfused with Krebs-Ringer solution containing phosphate (P_i) (1,2). Recently, it has been suggested by Lyon et al. (3) that >90% of the DQF ^{23}Na signal in perfused liver arises from intracellular Na^+. They have reported that addition of the shift reagent (SR), $Dy(PPP_i)_2$, to liver perfused with P_i containing Krebs-Henseleit buffer results in a large, shifted DQF signal of unknown origin having a greater amplitude than the total signal before addition of SR. To further investigate this phenomenon we have examined DQF ^{23}Na spectra of rat hearts perfused with several different HEPES-based solutions (P_i-free, P_i-free with SR, P_i containing, and P_i containing with SR). DQF ^{23}Na spectra were acquired using a $90° - \tau/2 - 180° - \tau/2 - 90° - \delta - 90° - t$ (acquisition) pulse sequence and 256 step phase table. The preparation time, τ, was set to 4, 8, or 16 ms, δ was fixed at 20 μs, and 4096 transients were signal averaged.

HEPES-based buffer alone did not give rise to a DQF ^{23}Na signal at any of the τ values studied and addition of P_i and/or SR did not alter the spectra. Thus, any DQF ^{23}Na signal observed in the perfused heart must arise from intracellular Na^+ or extracellular Na^+ interacting with membrane surfaces. Comparison of DQF ^{23}Na spectra of the heart before and after perfusion with SR containing media demonstrated a considerable contribution from extracellular Na^+ to the observed DQF signal (Fig. 1). The presence of SR did not induce an increase in the total DQF signal of the perfused heart in either P_i-free or P_i-containing media. In addition, the presence of P_i in the perfusing solution (SR-free or SR-containing) did not significantly alter the DQF spectra of the perfused heart demonstrating that P_i has no measurable influence on the extracellular contribution to the DQF ^{23}Na spectrum of the perfused heart. It is possible that the effect of P_i observed in perfused liver might result from interactions with a microprecipitate which forms when SR is added to bicarbonate-based buffers.

Linda A. Jelicks Raj K. Gupta

1. Jelicks, L. A. and Gupta, R. K., J. Magn. Reson. 81 586-592 (1989).
2. Jelicks, L. A. and Gupta, R. K., J. Biol. Chem. 264 15230-15235 (1989).
3. Lyon, R. C., Ruttner, Z., and McLaughlin, A. C., SMRM 10th Annual Meeting Abstract p. 633, Aug. 1991.

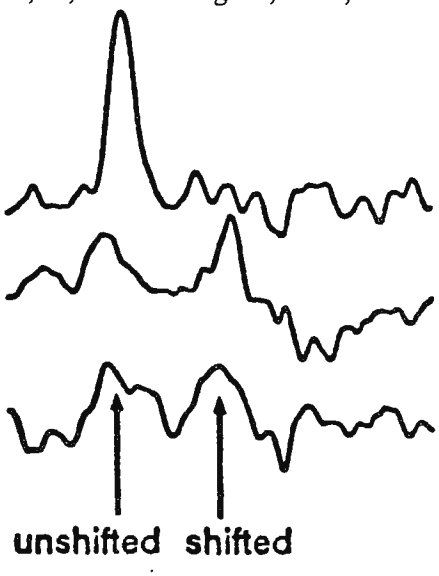

Fig. 1: DQF ^{23}Na NMR spectra of a rat heart before (upper trace) and during perfusion with P_i and SR (middle trace) and P_i- free and SR (lower trace) containing media. τ was set at 8 ms.

UNIVERSITY OF DELAWARE
Department of Chemistry and Biochemistry

Cecil Dybowski
Professor

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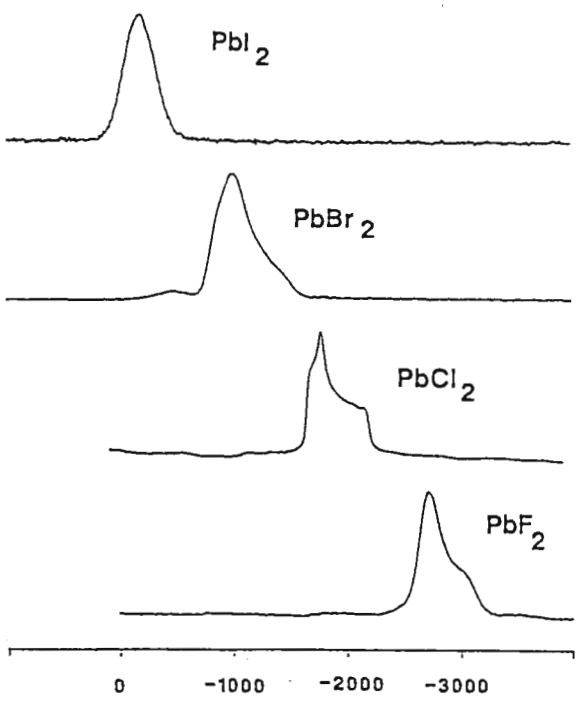
October 24, 1991
(received 10/28/91)

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



Solid-State Lead-207 Chemical Shifts

Dear Barry,

I received with delight your "reminder" of our obligation to TAMUNN. Recently we have been investigating (and sometimes reinvestigating) the NMR properties of solid lead compounds. As an example, I show spectra of the lead halides. What is striking about these spectra is the wide range over which the resonance of Pb^{2+} may occur, the rather significant anisotropies in the cases of $PbBr_2$, $PbCl_2$, and PbF_2, and the fact that the line shape of the iodide is noticeably different from the others. This latter fact is easily explained by a difference in the unit cell of PbI_2. In addition to these materials, we have investigated many others lead-containing materials including the many oxides of lead, and we find the NMR shift is extremely sensitive to environment, with the range being +11000 to -5000 ppm relative to tetramethyllead. Because of this wide range, the major problem we have encountered in this project is knowing where to look for the resonance of each sample we examine!

For interested readers of TAMUNN I point out the following: the Sixth International Symposium on Magnetic Resonance in Colloid and Interface Science is scheduled to be held in Florence, Italy June 22 - 26, 1992. For further information on this meeting, people should contact Professor Giacomo Martini, Chairman, 6th International Symposium on Magnetic Resonance in Colloid and Interface Science, Department of Chemistry, University of Florence, Via G. Capponi 9, 50121 Firenze, Italy.

Yours truly,

Cecil

Cecil Dybowski
Professor

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Spurious Outputs: −75dBc
Phase Noise: −75dBc (0.5Hz-15KHz)

Freq. St'd: OCXO, TCXO, Ext.
Interface: BCD par. or GPIB
Price: $5,125.00*

PTS 160

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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PTS 250

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 310

Range: 0.1-310 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); Type 2 −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
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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)

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Spurious Outputs: −65/−60dBc (typ/spec)
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DEPARTMENT OF CHEMISTRY

"A Bias in NMR R Factors"

Barry Shapriro, Editor
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Thursday, October 17, 1991
(received 10/26/91)

Dear Barry:

We have recently been evaluating dynamical structures for DNA on the basis of their agreement with experimental NMR data. Using the procedures we have recently described[1] various molecular dynamics simulations have been used to predict the observable NOE buildup curves and the predicted and theoretical data compared.[2] To assess the quality of the fits between the experimental and theoretical data we first used the "NMR R factor" given by[3-5]

$$R(\tau_m) = \sum_{ij} | E_{ij}(\tau_m) - T_{ij}(\tau_m) | / \sum_{ij} E_{ij}(\tau_m)$$

with $E_{ij}(\tau_m)$ being the experimental intensity of the cross-peak between protons i and j at mixing time τ_m and $T_{ij}(\tau_m)$ being the theoretical intensity. The R factor for the entire mixing time series is given by

$$R = \sum_{m} \sum_{ij} | E_{ij}(\tau_m) - T_{ij}(\tau_m) | / \sum_{m} \sum_{ij} E_{ij}(\tau_m).$$

This method is based on the R factor used in crystallography and is probably not entirely appropriate for comparing the predicted and observed NOE data for duplex DNA (or for proteins). It is noted that the net intensity of a diffraction pattern is (more or less) independent of the internuclear distances of the scattering centers whereas the net intensities of the NOEs are strongly dependent on the internuclear distances.

The NMR R factor for the case of having an experimental NOE of magnitude 3 and a theoretical NOE of magnitude of 1 is 2/3. The NMR R factor for the case of having an experimental NOE of magnitude 1 and a theoretical NOE of magnitude of 3 is 2. This simple example points out that the NMR R factor favors structures in which the experimental result is larger than the theoretical over those for which the experimental result is smaller than the theoretical. We can think of no justification for this bias. Our analysis of the NMR R factors for the dynamical structures of duplex DNA indicate that this bias can be quite significant. Therefore, we have examined some alternatives to the NMR R factor approach which do not have this

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Extension . 2401
Our reference HB/mjd
Your reference

Date 29th October 1991
(received 11/8/91)

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Dear Professor Shapiro,

Integrals in ^{13}C NMR

A recent paper by Alex Bain *et.al.*[1] encouraged the use of peak heights in quantitative NMR analysis and helped me to recall Frank Anet's earlier note on accurate integration in a TAMU NMR Newsletter.[2]

Our own work dates from about 1972 and has been largely concerned with the determination of conformational equilibrium constants from ^{13}C NMR spectra recorded in the range 130K to 170K. The requirement to use the same solvent when comparing equilibria in a series of closely related molecules has imposed limitations, especially for polar molecules which have a restricted solubility in the rather non-polar solvents inevitably required for low temperature observation. In such cases the range of temperatures possible is limited and a completely "frozen" spectrum cannot always be achieved. The use of peak heights is in this case ruled out, as signal widths show substantial differences.

As is well known, signal areas in low temperatures ^{13}C spectra do accurately reflect molecular proportions, provided the measuring conditions are appropriate, provided the carbon atoms compared are structurally identical and provided the carbons possess the same numbers of hydrogen atoms.[3] We adopted this method of analysis in preference to methods based on chemical shifts or coupling constants because it is direct, and requires no "model compounds", the reliability of which will always be questionable. Base-lines in ^{13}C spectra are generally excellent and a base-line correction is unnecessary. Nevertheless, we prefer to compare signals which are reasonably close in shift, provided they do not actually overlap. Signals are expanded to a scale of about 5 to 10Hz/cm and areas are determined by using a hand planimeter, the measurements being repeated 5 times and the results averaged. The procedure is tedious and requires a steady hand, but it is one in which we have a great deal of confidence.

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on p. 54

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bias. We have submitted a manuscript to *J. Magn. Reson.* describing these alternative methods.

1. J. M. Withka, S. Swaminathan, D. L. Beveridge and P. H. Bolton, *J. Am. Chem. Soc.* **113**, 5041 (1991).
2. J. M. Withka, S. Swaminathan, J. Srinivasan, D. L. Beveridge and P. H. Bolton, *Science* **00**, 000 (1991).
3. C. Gonzalez, J. A. C. Rullmann, A. M. J. J. Bonvin, R. Boelens and R. Kaptein, *J. Magn. Reson.* **91**, 659 (1991).
4. E.P. Nikonowicz, R.P. Meadows, and D. G. Gorenstein, *Biochemistry* **29**, 4193 (1990).
5. M. Gochin and T.L. James, *Biochemistry* **29**, 11172 (1990).

Sincerely,

Jane Withka Jayshree Srinivasan Philip Bolton

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The r.m.s. deviations in derived equilibrium constants are in the range of 1.5-4% - generally much greater than that required by Frank Anet in his work. The errors are largely dependent on the extent of intrusion of noise into the peak outline and the uncertainty in the choice of base-line. In the most favourable cases of excellent signal to noise, we also use instrumental integration and average the results with those from hand *planimetry*.

Yours sincerely,

H. Booth

References

1. A.D. Bain *et.al.*, *Can. J. Chem.*, **1991**, *69*, 1189.
2. F.A.L. Anet and D.J.O'Leary, *TAMU Newsletter*, **1989**, *366*, 36.
3. *cf.* H. Booth and M.L. Josefowicz, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 895.

Gradient Enhanced Spectroscopy SWAT

GE introduces the use of Switched Acquisition Time (SWAT) gradients to achieve pure phase 2D spectra with quadrature detection in both the acquisition (ω_2) and evolution (ω_1) dimensions without any phase cycling and without an additional set of t_1 data.

One example of a pure phase gradient enhanced COSY spectrum of a solution of 2,3-dibromopropionic acid in benzene-d6 is shown in Fig. 1. SWAT gradients and a single acquisition per block were used. Data was collected on an Omega 300WB with Microstar actively-shielded gradients. A 5mm inverse probe was built for use within the gradient coils.

Digital resolution of 1.2 Hz in ω_1 and 2.4 Hz in ω_2 was achieved by collection of a 512 x 512 matrix with t_1 evolution time of 840ms and a t_2 acquisition time of 420ms. A single acquisition per t_1 evolution data block and an average recycle time of 1.84s resulted in a 15 minute total collection period.

Since the SWAT gradient method encodes the necessary information in a single t_2 acquisition time, it avoids the collection of additional data blocks required by traditional pure phase methods. This time efficiency is especially important for collection of large multidimensional data sets.

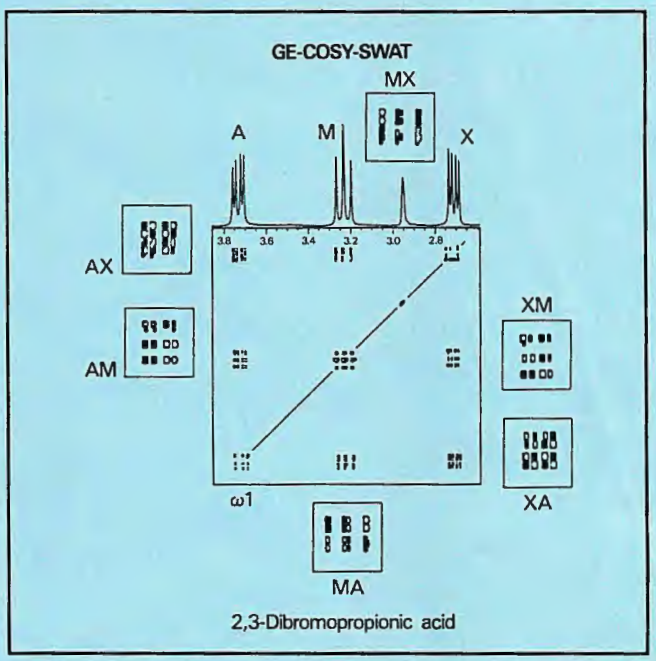

Fig. 1

Contour plot of a 300 MHz pure-phase COSY spectrum of a solution of 2,3-dibromopropionic acid in benzene-d6 acquired with only a single acquisition per t_1 evolution time increment using the GE-COSY-SWAT method. Cross peaks are shown in expanded insets with positive peaks as darkened contours and negative peaks as open contours. A one dimensional spectrum is plotted across the top of the 2D spectrum.

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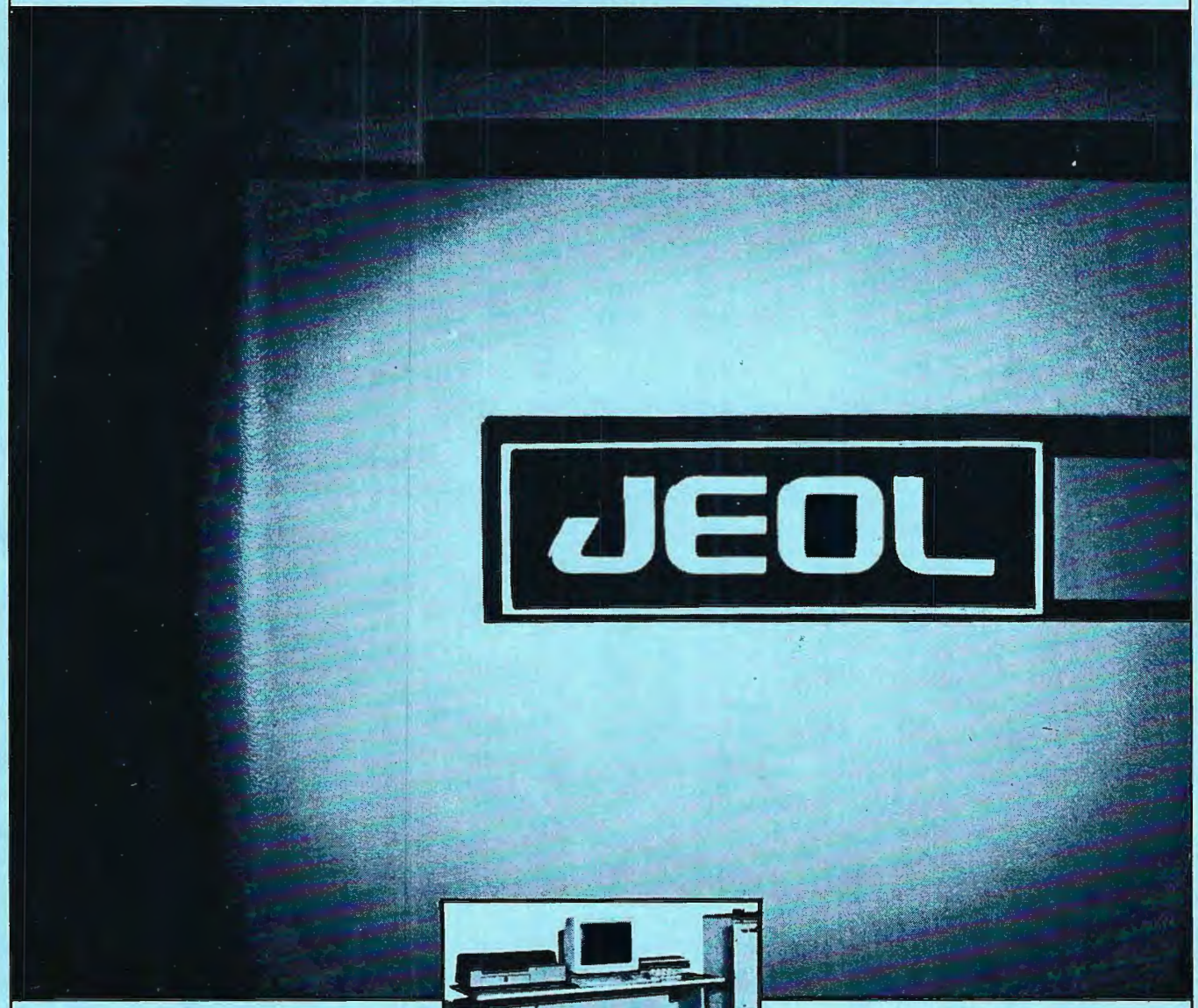
Of all the advanced technology on this research-level NMR, this may be the most important piece of hardware.



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