TEXAS A&M UNIVERSITY

NMR NEWSLETTER

NO. 332

MAY 1986

(continued on page 1)

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TEXAS A&M UNIVERSITY

NMR NEWSLETTER

All Newsletter Correspondence
Should be Addressed to:

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

DEADLINE DATES

No. 334 (July) ---------- 25 June 1986

No. 335 (August) ----------25 July 1986

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FORTHCOMING NMR MEETINGS (Additional listings are solicited)

Scuola Internazionale di Fisica E. Fermi: The Physics of NMR Spectroscopy in Biology and Medicine - June 24-July 4, 1986; Varenna, Italy; Chairman: Professor B. Maraviglia, Dipartimento di Fisica, Universita degli Studi, "La Sapienza," P. le Aldo Moro, I-00185 Roma, Italy.

International Society of Magnetic Resonance (ISMAR), 9th Meeting - June 29-July 5, 1986; Hotel Gloria; Rio de Janeiro, Brazil. Chairman: N.V. Vugman, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil.

U.S.-Latin American Workshop on Recent Developments in Organic and Bioorganic NMR - July 7-11, 1986; Campinas, Brazil; see Newsletter No. 323, p. 59.

28th Rocky Mountain Conference - August 3-7, 1986; Radisson Hotel; Denver, Colorado; Conference Chairman: R. Barkley, CIRES, University of Colorado, Boulder, Colorado 80309, (303) 492-1158. Abstract Deadline: March 21, 1986. NMR Chairmen: J. Haw, Dept. of Chemistry, Texas A&M University, College Station, Texas 77843, (409) 845-1966, and F. Miknis, Western Research Institute, Box 3395, University Station, Laramie, Wyoming 82071, (307) 721-2307.

XXIII Congress Ampere on Magnetic Resonance - September 15-19, 1986; Rome, Italy; XXIII Congress Ampere, Dipartimento di Fisica, Universita de Roma, "La Sapienza," P. le Aldo Moro 5, I-00185 Roma, Italy.

Federation of Analytical Chemistry and Spectroscopy Societies (FACSS XIII) - September 28-October 3, 1986; St. Louis, Missouri; Program Manager: Dr. Sydney Fleming, FACSS (Titles), 24 Crestfield Road, Wilmington, Delaware 19810.

1986 Eastern Analytical Symposium - October 20-24, 1986; Hilton Hotel, New York; see p. 79 and Newsletter No. 329, p. 23.

TABLE OF CONTENTS (continued)

THE UNIVERSITY OF ROCHESTER
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601 ELMWOOD AVENUE
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DEPARTMENT OF RADIATION BIOLOGY
AND BIOPHYSICS

January 31, 1986

Polymer Mobility Monitored via Spin Echoes
in Solid State Cross-polarization ^{13}C Spectra

Dear Barry:

In an effort to characterize molecular motions in polymer systems via ^{13}C resonance and relaxation, we recently studied polyvinyl acetate. The ^{13}C lineshape and ^{13}C spin-lattice relaxation times in the Zeeman and rotating frames were measured on dry and water-treated samples. Although these measurements have provided some understanding of the dynamical state of the polymer, characterization of motions on a time scale of several ms to tens of ms was not fully established (Macromolecules, in press).

Recently Zilm (K. W. Zilm, Abstracts of the FACSS 12th Annual Meeting, September 29 - October 4, 1985, Philadelphia, Abstract #135) has reminded us that the Fourier transform of the entire echo train in a conventional Meiboom-Gill - Carr-Purcell type of experiment yields sharp lines separated by the inverse of the cycle time and the peaks of these lines outline the shape of the inhomogeneously broadened line (A. N. Garroway, J. Magn. Reson. 28, 365, 1977). The experiment has a number of similarities to the conventional spin echo measurements of translational diffusion except that the role of the magnetic field gradient is filled by the magnetic anisotropy in the system. We show the spectrum of cadmium acetate collected this way in Figure 1B and the usual non-spinning spectrum in Figure 1A. The ^{13}C spectrum is characterized by rigid carboxyl and methyl tensors with the line width of individual peaks of about 20 Hz.

We show the same experiment done on dry and wet polyvinyl acetate in Figures 1C and 1D. Dry polyvinyl acetate is similar to the rigid system. The widths of individual lines in the echo spectra are typically 20-30 Hz, similar to the rigid Cd-acetate. The ^{13}C T_2 is long compared to the spacing, 2τ, between the 180 degree pulses so that the magnetization echoes dephase over the acquisition time. On the other hand, for the same value of τ, the magnetization dephases before the first echo for the carboxyl carbon when water is added to the polymer. The FT spectrum, therefore, yields no sharp lines and essentially yields the usual powder pattern. By monitoring the dephasing of the ^{13}C magnetization due to the motional modulation of the chemical shielding anisotropy as a function of the pulse spacing, τ, one has a convenient handle on relative slow motions.

We think this is a particularly clear application and demonstration of Kurt's idea.

Sincerely,

Robert G. Bryant

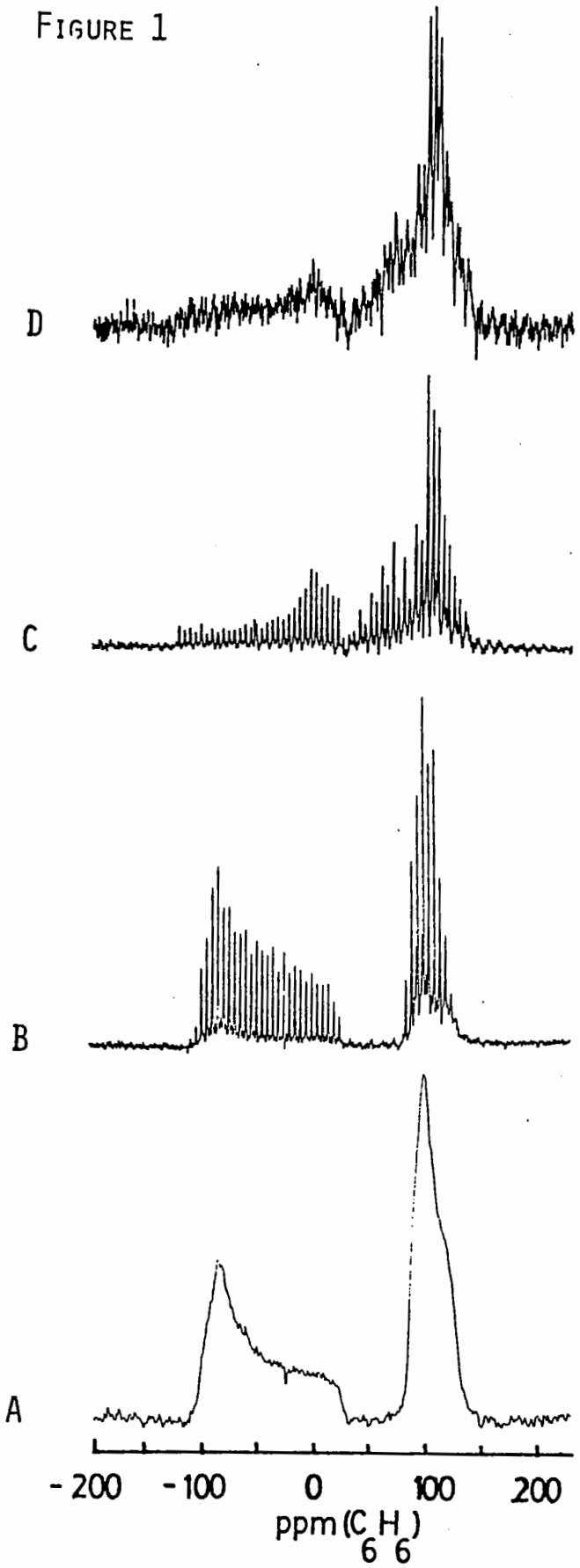
S. Ganapathy

Scott D. Kennedy

Scott Swanson

P. Mark Henrichs

FIGURE 1



ALL SPECTRA TAKEN AT 4.7 TESLA AND ROOM TEMPERATURE.

"WET" POLYVINYL ACETATE
(τ =2 MSEC)

DRY POLYVINYL ACETATE
(τ =2 MSEC)

CADMIUM ACETATE DIHYDRATE
(τ =2 MSEC)

CADMIUM ACETATE DIHYDRATE
(NORMAL CP SPECTRUM)

BERLEX Laboratories, Inc.
Subsidiary of Schering AG, West Germany

March 12, 1986

Dear Barry:

I have received my first ever "pink slip" warning from you and I can truly say it is every bit the shattering experience that I had heard from others that it was. As it turns out, there are several things that I would like to submit to TAMU Newsletter, but, for a variety of reasons, I cannot at this time. Accordingly, I will discuss something perhaps a bit more mundane, but which has turned out ot be useful in our laboratory.

As you know, the interpretation of complex COSY spectra can get to be quite confusing in the middle of the process of making assignments. [A corollary to this is that everything is as clear as a bell once the work is finished]. To help keep things straight, I have written a simple computer program which performs a crude simulation of a COSY spectrum. The inputs to the program are the chemical shifts of the various protons involved and the "connections", that is, the coupling relationshps that give rise to cross peaks. The output consists of a low resolution plot of the COSY spectrum with the centers of the peak clusters indicated by some plotting character. In the cases shown here I have used an "●" as the plotting character.

Of course the calculations involved here are extremely simple and can easily be done by hand. Having the data in the computer is convenient, however, allowing the "operator" to interchange chemical shift assignments in order to verify that said assignments are "unique".

An indication of how the program works is shown in Fig. 1. Protons 1,2 and 3 having the chemical shifts and "connections" indicated give rise to the plot shown in Fig. 1(a). Interchanging the chemical shift assignments of protons 2 and 3 produces the spectrum in Fig. 1(b).

Such simple spectra are unlikely to cause anyone any problem, but the COSY spectrum (partial plot) shown in Figure 2(a) (due to 19 protons from each of two diastereomers, only one of which is plotted in the simulation) might prove to be more difficult. The effect of interchanging just one pair of resonance assignments is shown in Fig. 2(b) and Fig. 2(c). During the development of the final interpretation, such plots were useful in eliminating alternative possibilities.

The program is written in BASIC to run on a Commodore 64. Since no special Commodore commands are used, it should be possible to adapt it to almost any computer. Of course, it would be a better program if a first order NMR simulation package were added and then a lineshape program and then .... Perhaps in the fullness of time this will come to be, but not yet.

Sincerely,

C. Anderson Evans
Staff Scientist,
Analytical

TITLE: Getting Cosy With COSY
[Title supplied by the Editor]

110 East Hanover Avenue, Cedar Knolls, New Jersey 07927 (201) 540-8700 Telex 136354

Figure 1(a)

Proton	δ	Coupled to
1	1	2
2	2	1,3
3	3	2

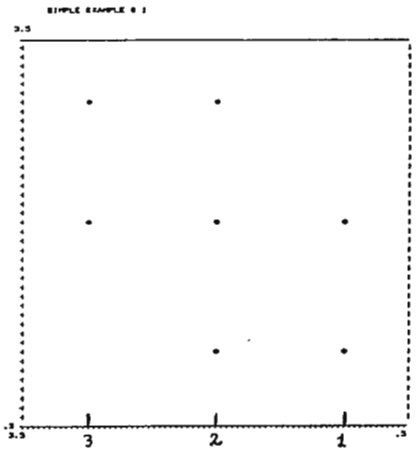


Figure 1(b)

Proton	δ	Coupled to
1	2	2
2	1	1,3
3	3	2

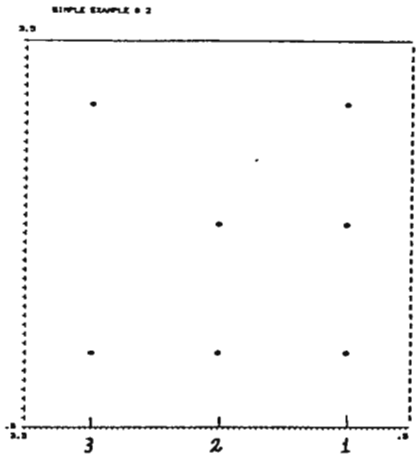
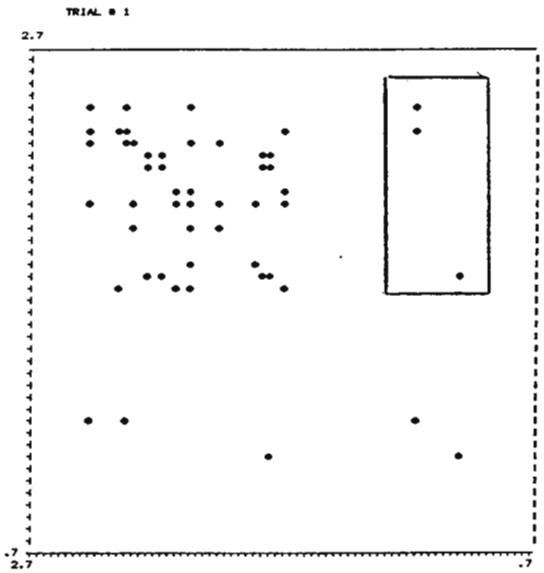


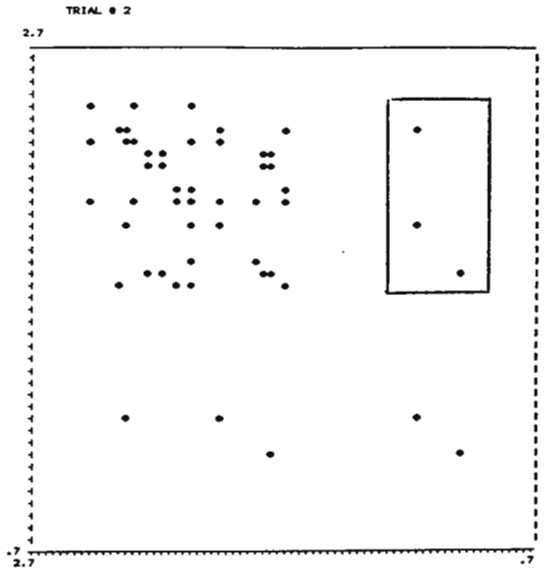
Figure 2

(a)

(b)



(c)



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UCD NMR FACILITY DAVIS, CALIFORNIA 95616

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

4/2/86

Regional Resource For In-Vivo NMR

Dear Professor Shapiro:

We would like to announce that part of the UCD NMR Facility has been formed into an NIH Regional Resource for in-vivo NMR. We have available a horizontal 1.9T/31 cm clear-bore ORS spectrometer as well as Nicolet 4.7T/8.9 cm and 8.5T/5.5 cm systems.All of the spectrometers are multi-nuclear and are currently employed for in-vivo research. Areas of current study in brief include P31, C13, F19, and Na23 via surface and conventional coils on systems ranging from phantoms to perfused cellular suspensions to mice, rats, rabbits, etc., up to human limbs on the 1.9T.

As a Regional Resource the utilization of these facilities by qualified off-campus researchers is available, with use of the 1.9T provided without recharge and the 4.7T and 8.5T available at 50% of our current recharge rate. We are also able to provide some assitance and consultation from our staff to assist users. Later this year the 1.9T will be upgraded to have imaging, and we are currently negotiating the purchase of a 7T/15-17 cm. horizontal spectroscopy/imaging system to be delivered in 1987, which would also be available to Regional Resource users. Those wishing further information may contact Carol Witham at 916-752-2927 or Jeff de Ropp at 752-7677.

Sincerely,

Morton Bradbury

E. Morton Bradbury, Professor
Principal Investigator

Jeffrey S. de Ropp

Jeffrey S. de Ropp
UCD NMR Facility

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Unique Life Support System for Tissue Culture

March 26, 1986

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

Dear Professor Shapiro:

Your readers who are interested in working with cells in tissue culture may find our experience helpful. We have developed a unique life support system for tissue culture that can be used in a high field NMR system.

In the past several years we have been studying neuronal type cells in tissue culture, using 31P NMR with a Bruker 360 WB spectrometer. The life support system was first reported by us in 1981 (1). Since then attention to detail and a change in sample holder have resulted in a much improved signal (2). Requirements for a system such as this one shown in the figure are to keep cells healthy and metabolically stable for a long time, free from cell contamination during NMR measurements, and, of course, to have reasonably good NMR sensitivity with good resolution.

The cells we work with are mostly anchorage-dependent cells such as neuroblastoma, glioma, and dissociated rat brain cells. NMR samples are prepared by growing cells with traditional tissue culture techniques, seeding the cells on to microcarriers (2), allowing time for attachment (approximately 30 minutes) and then pipetting with a wide mouth pipet the microcarriers with cells attached into a sample holder and closing the system. The technique of how to get the cells on the microcarriers varies with the cell type. We grow C3HT101/2 cells on microcarriers for 5-7 days as compared to the neuroblastoma cells where only 30 minutes is allowed for attachment. The type of microcarriers is also cell type dependent. Biosylon is an excellent choice for C3HT101/2 cells, and Cytodex III has been found best for neuroblastoma cells. The quantity of these cells needed to fill the volume of the sample holder (6 ml) can be obtained

from 30 nearly confluent 100 mm plates. The volume fraction the cells occupy in the holder is at most 10%.

The heart of the system is the sample holder. It now consists of two silicone corks (#2) cut down as shown in the drawing. In one end a cone is cut out and a hole is made coaxially in the cork with an ice pick. A length of Teflon tubing which has had the last half inch roughened with sand paper is forced through the hole and held in place with Dow Corning silicone rubber adhesive. The end of the cone is covered with nylon mesh and is held in place with silicone rubber adhesive. The cone facilitates a homogenous flow of liquid through the sample. Air bubbles trapped in the holder can be removed by inserting a hypodermic syringe through the cork. We pump between 3 and 4 ml per minute through the system.

The system as we use it today is made of brass, nylon, Teflon, silicone rubber and glass. Everything is autoclavable. The weak link in the sterile technique is threading the sample holder through the R.F. coil and loading the cell-microcarrier complex into the sample holder. This is done in a sterile hood. The result is that we have gone 20 to 30 days without contamination and when contamination appears as fungus or yeast, a 31P peak is seen at approximately 22 ppm, the position for the polyphosphate store for these contaminants. When E. coli infects the sample, the signal intensity drops dramatically.

One of the criteria for a good system has been one which allows the intracellular and extracellular orthophosphate to be resolved, thus allowing intracellular pH and phosphate concentration to be determined. This limits the size of the sample to 20 mm in diameter by 20 mm in length. The signal to noise was good enough to obtain a signal in 2 minutes when using a repetition time of 0.5 seconds. With a 3 second repetition rate, the spectrum below was obtained in one hour. This spectrum has been line broadened with an exponential multiplication factor of 2.5 Hz. We used a single-turn coil in a homemade probe. Shimming was done on water. The proton pulse was connected to the 31P port of the probe and this proved to give a fine shimming signal. The 31P signal is too weak for shimming.

Yours sincerly
Paul Glynn
(Paul Glynn)

References:

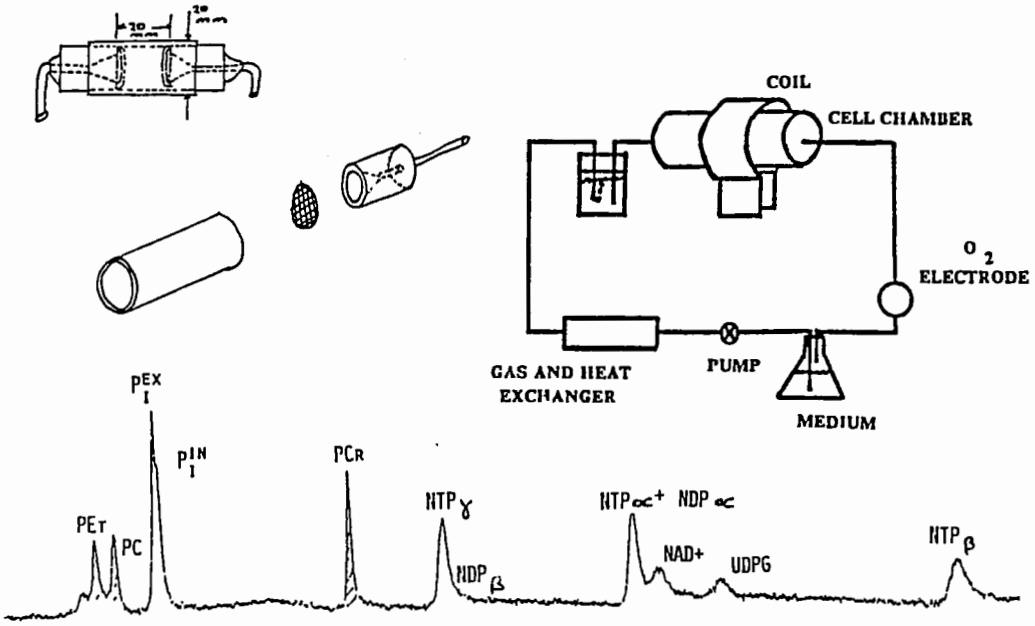
1. Ugurbil, K., Guernsey, D.L., Brown, T.R., Glynn, P., Tobkes, N., and Edelman, I.S. 31P NMR studies of intact anchorage-dependent mouse embryo fibroblasts. (1981) Proc. Natl. Acad. Sci. USA 76, 1800-1804.

2. Thesis: 31P NMR of neuronal cell systems in tissue culture. Submitted to CUNY, Spring, 1986.

3. KC Biological, Technical Service Department, 1-800-255-6032

4. Biosylon by NUNC, distributed by Grand Island Biological Co. Grand Island, NY 14072

5. Pharmacia Cytodex, 800 Centennial Avenue, Piscataway, NJ 08854 (They have an excellent book, "Microcarrier cell culture principles and Methods.")



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Our file: 600/301/11/1 Your file:

Professor Bernard L Shapiro
Department of Chemistry
Texas A & M University
COLLEGE STATION
TEXAS 77843
USA

17 MAR 1986

Dear Professor Shapiro

NON-EQUIVALENCE OF $^3J_{exo,exo}$ AND $^3J_{endo,endo}$

The non-equivalence of the exo-exo and endo-endo vicinal proton-proton coupling constants in norbornanes is well established,[1] and was also rationalized theoretically.[2] Specifically, it was proved[2] by the use of NNBI[3] (Neglect of Non Bonded Interactions) calculations of the through-space contributions to $^3J(H,H)$ that the C-5,C-6--C-7 non-bonded interactions [type (a)] in bicyclo[2.2.1]heptane(I) reduce ^3J (endo,endo), whereas the ethylene bridge-ethylene bridge (C-5,C-6--C-2,C-3) interaction [type (b)] reduces the exo-exo vicinal coupling constant; $^3J(exo,exo) > {}^3J(endo,endo)$ in norbornane since interactions of type (a) predominate.

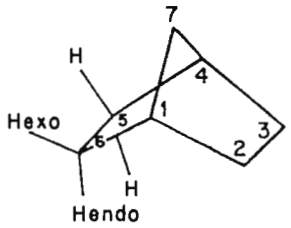
Non-bonded interactions of type (a) are also evident[4] in other rigid bicyclo[m.2.1]alkanes. A similar pattern to that in norbornane with regard to exo-exo and endo-endo vicinal proton-proton coupling constants is anticipated for bicyclo[3.2.1]octane(III) and bicyclo[4.2.1]nonane(V). A difference of 4-5 Hz between $^3J(exo,exo)$ and $^3J(endo,endo)$ for (III) and (V) was evaluated by INDO-FPT calculations, whereas the neglect of non-bonded interactions of type (a) reduces this difference to 1.3-1.4 Hz. Interactions of type (b) have no significant effect on $^3J(H,H)$. According to the INDO-FPT calculation for bicyclo[2.2.2]octane(II) and bicyclo-[3.2.2]nonane(IV) interactions of type (b) reduce $^3J(exo,exo)$.

Yours sincerely

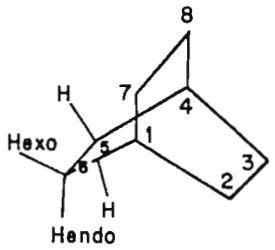
R Pachter P L Wessels

R PACHTER P L WESSELS

1. J.L. Marshall, S.R. Walter, M. Barfield, A.P. Marchand, N.W. Marchand and A.L. Segre, Tetrahedron, 32, 537 (1976).
2. F.A.A.M. de Leeuw, A.A. Beuzekom and C. Altona, J. Comp Chem., 438 (1983).
3. M. Barfield, J. Am. Chem. Soc., 102, 1 (1980).
4. R. Pachter and P.L. Wessels, J. Mol. Struct. (Theochem), 124, 25 (1985).



I



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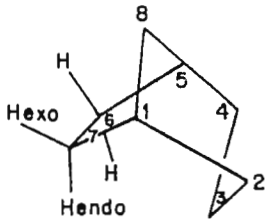
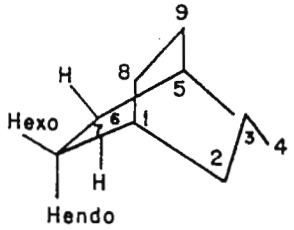
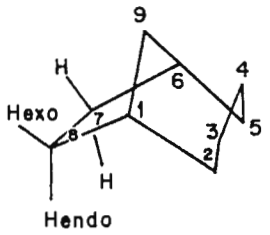


III



IV



V

^3J(H,H) INDO-FPT Calculated Coupling Constants (in Hz) in Molecules I-V

	I	II	III	IV	V
exo-exo					
	a 14.69	a 14.73	a 15.39	a 16.57	a 14.84
	b 14.44	b 16.26	b 15.27	b 18.63	b 14.83
	c 15.95		c 15.51		c 14.84
endo-endo					
	a 10.41	a 14.76	a 10.43	a 15.08	a 10.67
	b 14.06	b 16.28	b 13.98	b 15.45	b 13.43
	c 10.42		c 10.64		c 11.16

a unmodified calculation
b interactions of type (a) are neglected
c interactions of type (b) are neglected

The University of Iowa

Iowa City, Iowa 52242

Department of Chemistry

1047

25 March 1986

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

Title: CHROMIUM DPM: A SUPERIOR SPIN RELAXATION REAGENT

Dear Professor Shapiro:

In spite of the fact that Levy, et al. (1,2) have recommended the use of tris-(2,2,6,6-tetramethyl-3,5-heptanedionato)chromium(III) [alias tris-(dipivaloylmethanato)chromium(III), alias $Cr(DPM)_3$, mol.wt. = 601.5] as a spin relaxer, the use of the acetylacetonate chelate $Cr(AcAc)_3$ remains ubiquitous. This is a pity, because $Cr(DPM)_3$ is more soluble, more inert, and more predictable in its effects. The continuing preference for $Cr(AcAc)_3$ is presumably due partly to the fact that $Cr(DPM)_3$ is not commercially available, and partly to a mistaken belief that "$Cr(AcAc)_3$ must be the best possible general-purpose spin relaxer, because everyone else uses it."

I would like to bring to the attention of the NMR community the fact that Doyle (3) has worked out a good prep. for $Cr(DPM)_3$. The reference in Levy's 1975 paper is to a prep. for $Cr(AcAc)_3$, and that procedure will not work for $Cr(DPM)_3$.

We have routinely used $Cr(DPM)_3$ as a spin relaxer for the last seven years, primarily in ^{13}C and ^{15}N NMR studies. We like it because:

1. It is very soluble in both non-polar and polar solvents, except water. The concentration of $Cr(AcAc)_3$ required to achieve a desired effect with low-γ nuclei frequently exceeds solubility limits; we have not yet encountered this problem with $Cr(DPM)_3$, in spite of the fact that somewhat higher concentrations are required in the case of the DPM chelate.
2. The increase in $1/T_1$ is very predictable and even over the substrate molecule. $Gd(DPM)_3$ is not as good, because it occasionally yields dramatic differences in $1/T_1$ between different sites. Unlike chromium, gadolinium can expand its coordination sphere and sink its teeth into certain organic functional groups. Moderately large differential relaxations still occur with chromium chelates, but T_1 ratios have been observed to be closer to ideal (unity) with $Cr(DPM)_3$ than with $Cr(AcAc)_3$ (1). The fact that $Cr(DPM)_3$ is less specific in its effect is presumably due to better shielding of the electronic charges by the bulky t-butyl groups on the ligands.
3. So far, we have never observed any significant changes of NMR line position when $Cr(DPM)_3$ is added to a sample. The work of Levy, et al. (1) suggests that $Cr(AcAc)_3$ is more likely to yield measurable "shift-reagent" effects.

To illustrate the last two points, a $CDCl_3$ solution was prepared, containing 0.55 M TMS, 1.5 M benzaldehyde, and 1.5 M sec-butanol. ^1H and ^{13}C spectra were obtained. ^1H and ^{13}C T_1 measurements were then made on aliquots to which $Cr(AcAc)_3$ and $Cr(DPM)_3$ had been added, with the following results.

TABLE I. EFFECTS OF $Cr(AcAc)_3$ AND $Cr(DPM)_3$ ON ^{13}C NMR SIGNALS

NO CHELATE	15 mg/ml $Cr(AcAc)_3$ added		27 mg/ml $Cr(DPM)_3$ added	
δ ppm	δ ppm	$T_1 \pm \sigma$ sec	δ ppm	$T_1 \pm \sigma$ sec
192.38	192.40	0.898 ± 0.033	192.36	1.501 ± 0.056
136.48	136.50	1.008 ± 0.013	136.50	1.377 ± 0.047
134.48	134.53	0.861 ± 0.024	134.49	1.111 ± 0.048
129.75	129.79	0.910 ± 0.019	129.76	1.217 ± 0.013
129.01	129.07	0.869 ± 0.010	129.03	1.183 ± 0.015
77.75	78.06	0.510 ± 0.009	77.79	1.720 ± 0.035
77.40	77.71	0.508 ± 0.006	77.44	1.782 ± 0.068
77.05	77.35	0.504 ± 0.017	77.08	1.670 ± 0.040
69.18	69.18	0.813 ± 0.013	69.18	1.476 ± 0.042
32.06	32.08	0.933 ± 0.023	32.06	1.311 ± 0.017
22.85	22.89	0.851 ± 0.022	22.86	1.250 ± 0.031
10.06	10.07	1.105 ± 0.035	10.05	1.311 ± 0.055
TMS	TMS	1.353 ± 0.044	TMS	1.525 ± 0.053

Note that $Cr(AcAc)_3$ causes a +0.31 ppm shift of the $CDCl_3$ lines, and the ^{13}C relaxation times vary by as much as a factor of 2.7. $Cr(AcAc)_3$ appears to have a much stronger affinity for chloroform than for TMS. With $Cr(DPM)_3$, the "shift-reagent" effect on $CDCl_3$ is only 0.04 ppm, and the T_1's vary by a factor of 1.6 or less. If the concentrations of both chelates were increased so as to reduce the longest T_1's to 1 second, $Cr(AcAc)_3$ would still produce a shift nearly six times that produced by $Cr(DPM)_3$.

TABLE II. EFFECTS OF $Cr(AcAc)_3$ AND $Cr(DPM)_3$ ON ^1H NMR SIGNALS

NO CHELATE	15 mg/ml $Cr(AcAc)_3$ added		27 mg/ml $Cr(DPM)_3$ added	
δ ppm	δ ppm	$T_1 \pm \sigma$ sec	δ ppm	$T_1 \pm \sigma$ sec
9.97	9.97	0.0450 ± 0.0009	9.97	0.0888 ± 0.0012
7.85	7.85	0.0506 ± 0.0006	7.85	0.0871 ± 0.0009
7.58	7.59	0.0517 ± 0.0010	7.59	0.0756 ± 0.0013
7.49	7.49	0.0533 ± 0.0007	7.49	0.0790 ± 0.0009
3.71	3.71	0.0514 ± 0.0014	3.71	0.1170 ± 0.0026
3.20	3.19	0.0158 ± 0.0008	3.19	0.0521 ± 0.0011
1.47	1.48	0.0685 ± 0.0011	1.47	0.1140 ± 0.0017
1.17	1.17	0.0696 ± 0.0008	1.17	0.1164 ± 0.0007
0.92	0.92	0.0836 ± 0.0010	0.92	0.1143 ± 0.0008
TMS	TMS	0.1098 ± 0.0009	TMS	0.1161 ± 0.0007

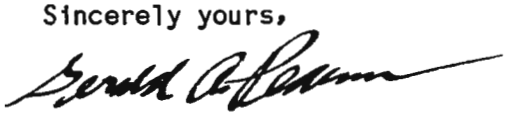
No significant line shifts appear in the proton data, but the T_1's ^{13}C exhibit much more dramatic differences than in the ^{13}C data. As in the ^{13}C results, $Cr(AcAc)_3$ yields the longest T_1 with TMS; the hydroxyl proton at 3.2 ppm relaxes 6.4 times as fast as the protons in TMS. With $Cr(DPM)_3$, the TMS protons relax at about the same rate as the aliphatic butyl protons, and the hydroxyl proton relaxes only 2.2 times as fast as the slowest proton.

When a spin relaxer is used to speed up polarization-transfer experiments (DEPT, INEPT, and especially 2-D X/H chemical shift correlations), a narrow range for the proton relaxation times is necessary for maximum sensitivity. If a ^1H T_1 is too long, sensitivity will be lost by incomplete relaxation during a short recovery delay. Too short a T_2, on the other hand, will cause signal loss during the evolution delays in the pulse sequence.

The point to be made here is not that $Cr(AcAc)_3$ is a poor general-purpose spin relaxer, but that $Cr(DPM)_3$ is better. We routinely use $Cr(DPM)_3$ for the same reason that we routinely use high-quality NMR tubes in superconducting spectrometers: to ensure that we obtain the best possible results.

I would like to thank Jack Doyle of this department for many helpful discussions, and for providing the NMR spectroscopists here with a 10-year supply of $Cr(DPM)_3$ in 1979. One of Jack's undergraduate students repeated the synthesis as a laboratory exercise, thus providing an additional 10-year supply.

Sincerely yours,



Dr. Gerald A. Pearson

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1. G. C. Levy, U. Edlund, and J. G. Hexem, J. Magn. Res., 19, 259 (1975).
2. G. C. Levy and R. W. Lichter, NITROGEN-15 Nuclear Magnetic Resonance Spectroscopy, Wiley, NY, 1979.
3. D. Stille and J. R. Doyle, "Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)chromium(III)", in INORGANIC SYNTHESIS, Vol. 24, J. Shreeve, Editor, Wiley, NY, 1986, in press. Requests for preprints should be addressed to Prof. Jack Doyle, Chemistry Department, University of Iowa, Iowa City, IA 52242.

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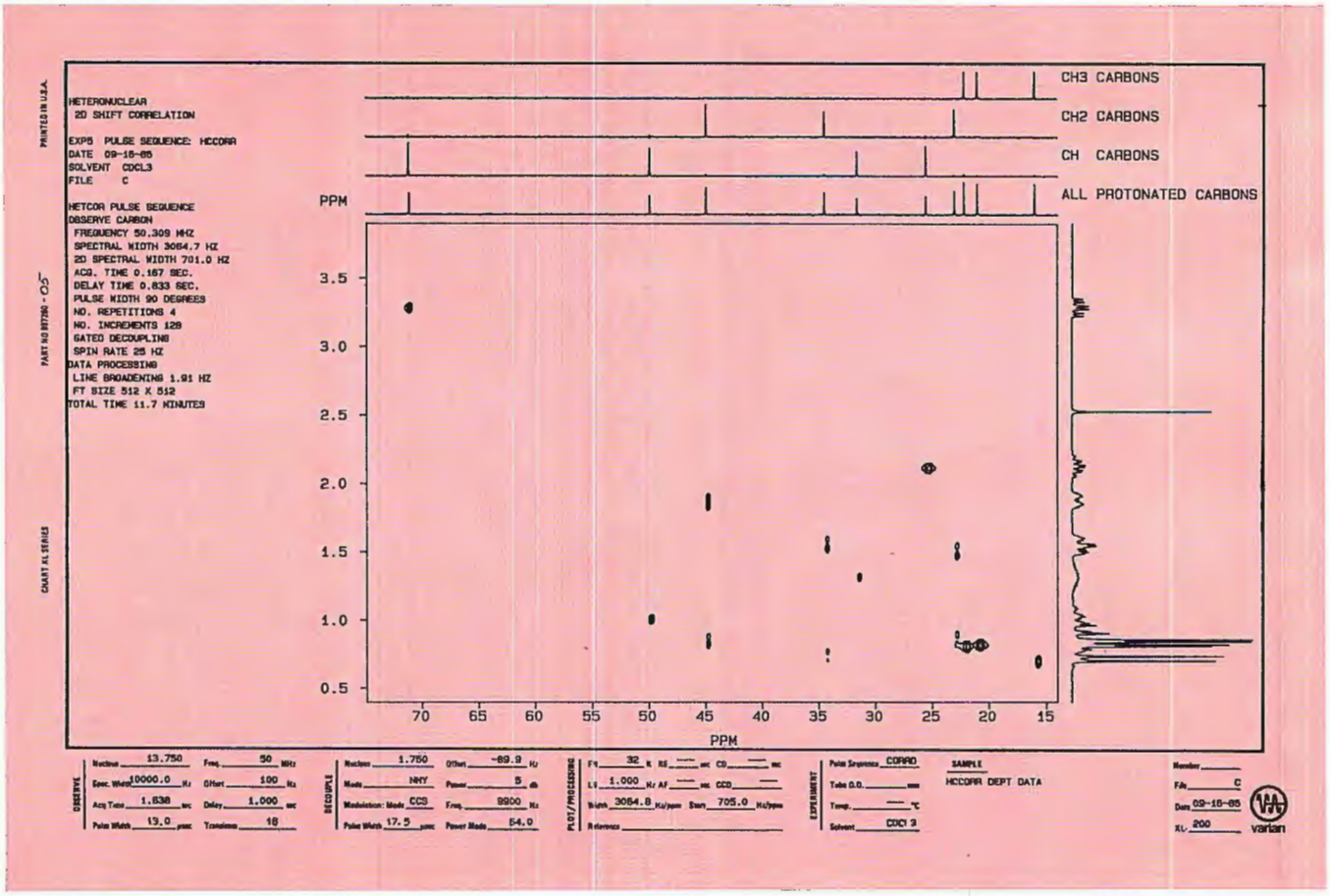

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DEPARTMENT OF CHEMISTRY

RIVERSIDE, CALIFORNIA 92521

March 28, 1986

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

Re: Resolution Limitation of Geminal Protons by CHORTLE

Dear Professor Shapiro:

I have some comments about the 1-D C/H chemical shift correlation technique (CHORTLE, see Fig. 1) proposed by G.A. Pearson in J. Magn. Reson. 64, 487 (1985). With regards to the resolution limitation for geminal protons, it has been claimed that "CHORTLE yields significant errors when geminal protons have small but non-zero differences in their chemical shifts (F' < 50 Hz)." But this doesn't have to be the case as optimal polarization transfer can be obtained by setting $2D_2$ = 3/2J, 5/2J, 7/2J, ..., (instead of 1/2J). Thus, extending proton chemical shift evolution time (for J = 125 Hz) to 12 ms, 20 ms, 28 ms, ... (instead of 4 ms). I have tested this scheme on a sample of 2-pentanol in acetone-d_6 using $2D_2$ = 12 ms, t = 10 ms and the results are shown in Table I. The accuracy of the calculated average proton chemical shift appears to be within 1 Hz and that of the calculated geminal proton chemical shift difference is a few Hz.

Although the loss of polarization transfer due to ^1H-^1H coupling and spin-spin relaxation during the extended evolution time cannot be avoided. In general, this loss is tolerable for $2D_2 \leq 20$ ms. The change of ^{13}C intensity with the length of D_2 for a gated-decoupling-refocused INEPT experiment on 2-pentanol using t_1 = 0, D_3 = 2 ms is illustrated in Fig. 2.

Please credit this contribution to the account of Dr. Robert Lee.

Sincerely,

C. S. Tzeng

C. Shue Tzeng
Staff Research Associate

CST/nc

Enclosure

Fig. 1. CHORTLE pulse sequence, J. Magn. Reson. 64, 487 (1985).

Fig. 2. ^{13}C intensities of 2-pentanol as a function of polarization time in INEPT. The numbering is as shown below:

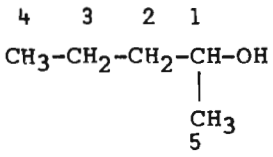

Table I. Comparison of Calculated and Observed ^1H Resonance Offsets[a] of 2-pentanol.

Position	F_0(cal)[b]	F'(cal)[b]	F_0(obs1)[c]	F_0(obs2)[d]	F'(obs2)[d]	Δ_0[e]	Δ'[f]
1	340.2	--	--	339.8		+0.4	
2	-358.4	29.6	--	-357.7	32.9	-0.7	-3.3
3	-359.2	22.4	--	-359.4	26.4	+0.2	-4.0
4	-505.3	--	-504.3	-504.9		-0.4	
5	-439.3	--	-438.1	-439.0		-0.3	

[a] In Hz, relative to the decoupler frequency except for F_0(obs1) which is relative to the transmitter frequency. F_0 is the average proton resonance offset, F' is the difference in resonance offsets of geminal protons.

[b] Calculated by CHORTLE.

[c] Obtained by ^1H NMR.

[d] Obtained by 2-D homo-decoupled hetero-shift correlation, (J. Magn. Reson. 53, 517 (1983)).

[e] $\Delta_0 = F_0(cal) - F_0(obs2)$.

[f] $\Delta' = F'(cal) - F'(obs2)$.

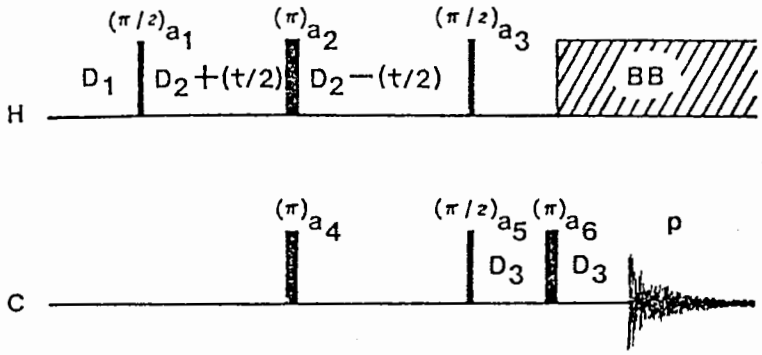
(π/2)a1
(π)a2
(π/2)a3
D1
D2+(t/2)
D2−(t/2)
BB
H
(π)a4
(π/2)a5
(π)a6
p
D3
D3
C

Fig. 1

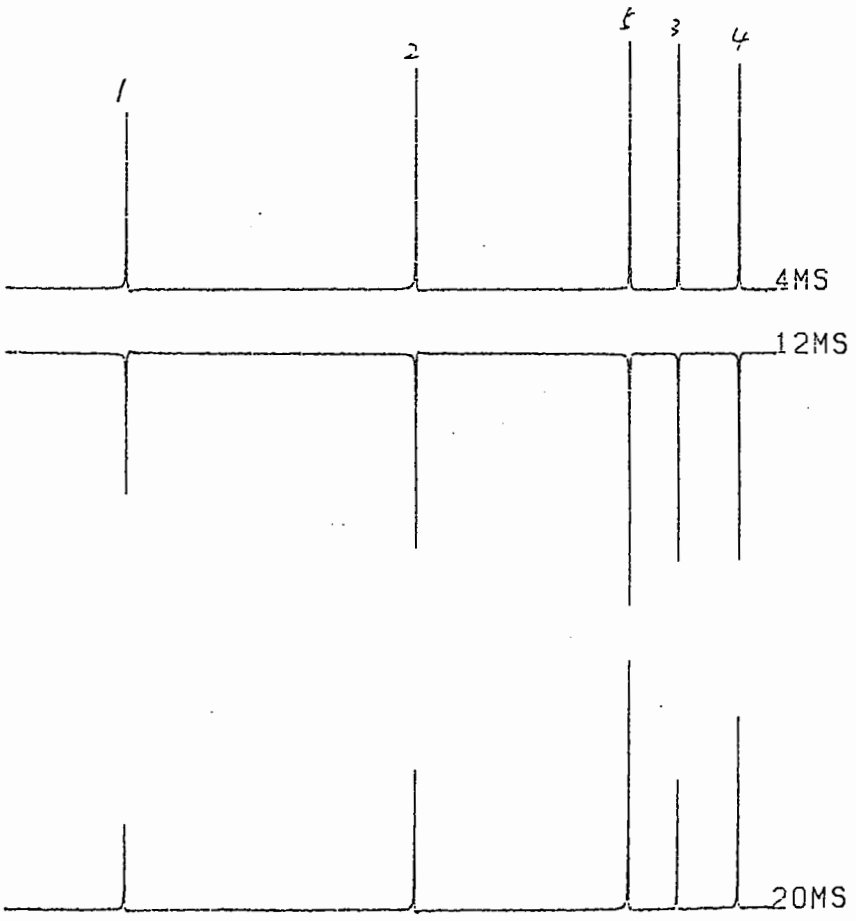
1
2
t
3
4
4MS
12MS
20MS

Fig. 2

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Rehovot 76 100, Israel רחובות 76100, ישראל

Isotope Department מחלקת איזוטופים
Direct phone : (08) 48 טלפון ישיר : 48(08)

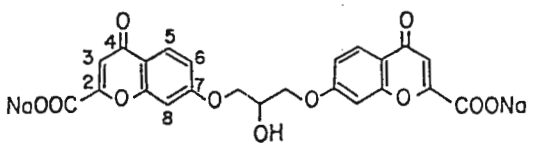
March 23, 1986

Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843-3255
USA

Dear Barry:

Unconventional Lyotropics

Lyotropic mesophases are formed in solutions of amphiphiles in water or polar organic solvents. Common amphiphiles consist of molecules with well segregated hydrophilic and hydrophobic regions, such as e.g. the alkyl chains and carboxylic groups in mono-soaps. Recently several compounds were found in which such a segregation of the polar and apolar regions does not occur (1-3). Our latest contribution to this list is 7,7'disodium cromoglycate (7,7' DSCG) which is an isomer of 5,5' DSCG.



Depending on the concentration and on the temperature, several phases are obtained with different ordering characteristics. A tentative phase diagram is shown in Fig. 1. Examples of NMR spectra of ^{2}H, ^{17}O and ^{23}Na, recorded on a CXP-300 spectrometer, from samples prepared with isotopically enriched water are shown in Fig. 2.

Besides the basic interest in such mesophases they may also be used as ordering solvents. At sufficiently low concentrations, they are quite fluid and may readily order water soluble species. This may particularly be useful for nuclei with large quadrupole interaction constants, e.g. ^{2}H, ^{17}O, ^{33}S, etc.

Please credit this letter to R. Poupko's account.

Sincerely yours,

D. Perahia Z. Luz

1. T.K. Attwood, J.E. Lydon, Mol. Cryst. Liq. Cryst. 108, 345 (1984).
2. D. Perahia, D. Goldfarb, Z. Luz, Mol. Cryst. Liq. Cryst. 108, 170 (1984).
3. I. Kustanovich, R. Poupko, H. Zimmermann, Z. Luz and M. M. Labes, J. Am. Chem. Soc. 107, 3494 (1985).

RP/sn

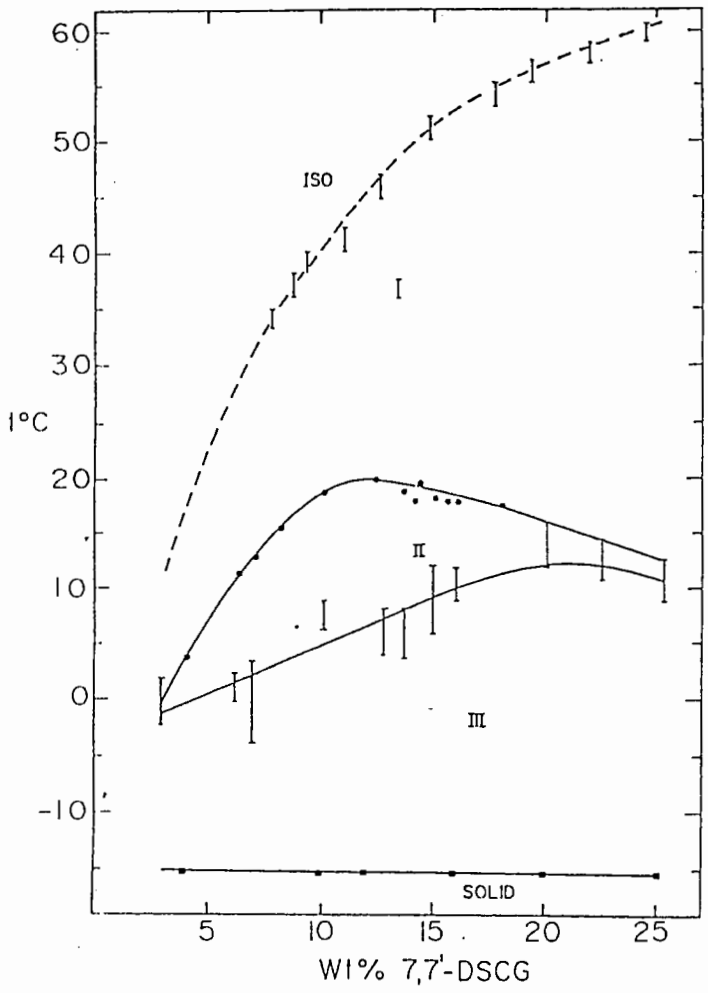


Fig. 1.
Phase diagram of aqueous solutions of 7,7'-DSCG. I, II and III are lyomesophases.

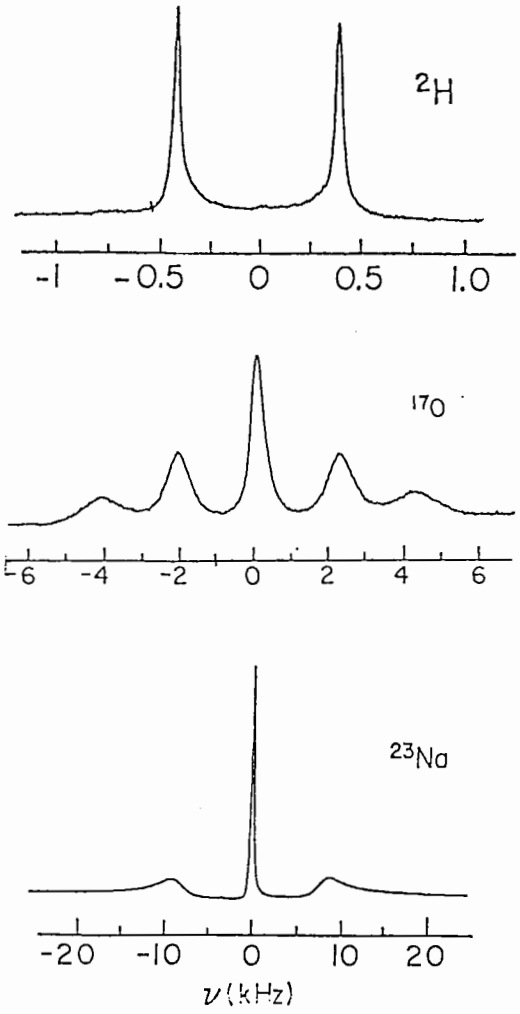


Fig. 2.
NMR spectra of a 12 wt.% solution 7,7'-DSCG in phase II (15°C), using appropriate isotopically enriched water.

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K1A 0R6

March 24, 1986

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

Difference n.O.e. Experiments in D_2O at 500 MHz

Dear Barry:

Structural and conformational studies of complex oligosaccharides by high resolution ^1H n.m.r. make considerable use of difference n.O.e. experiments, which for biologically interesting structures are most often conducted in deuterium oxide solution. After taking delivery of our A.M. 500 spectrometer we observed at times poor cancellation upon subtraction of the on and off resonance spectra, a problem not previously encountered at lower field strengths. Since the resonance frequency of the solvent lock in this case is highly temperature sensitive, stringent probe temperature control would be one answer to this problem. A more practical solution for many cases was found to be the addition of between 5-10% (v/v) of acetone-d_6 to samples dissolved in deuterium oxide. Difference n.O.e. experiments conducted on such samples using the acetone-d_6 lock provided the sought after stability and clean subtraction of unperturbed resonances in difference spectra.

As an example we show the spectrum of methyl 2-O-(2,6-dideoxy-α-L-arabinohexopyranosyl)-α-L-rhamnopyranoside (Figure A) and the n.O.e. difference spectra for experiments conducted using deuterium oxide (B) and acetone-d_6 (C) signals as the internal lock. Irradiation of the H-1' resonance results in readily observable n.O.e.'s on both vicinal H-2'e and H-2'a protons and across the glycosidic linkage to the aglyconic proton H-2.

Sincerely,

JR Brisson

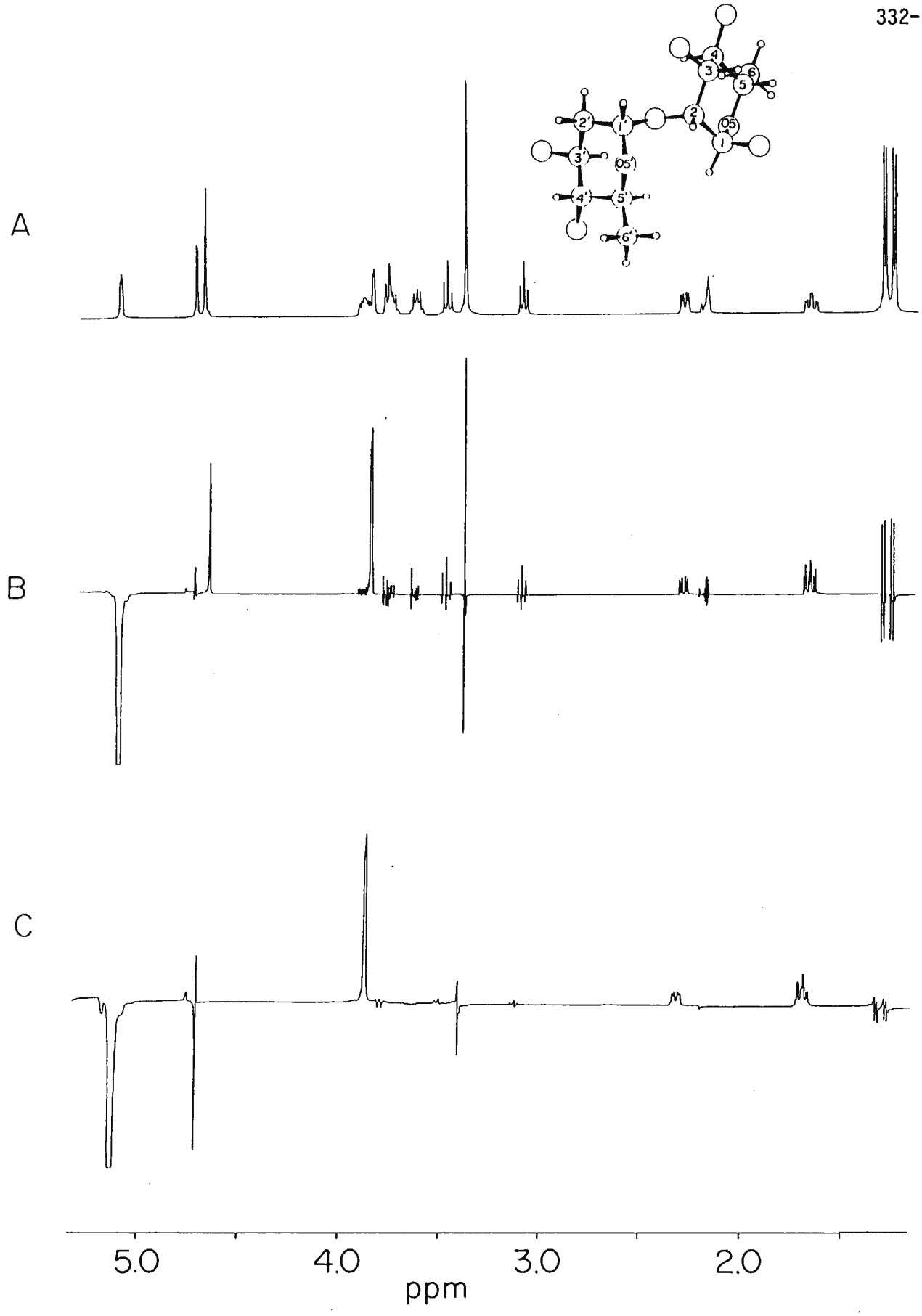
D. Bundle

and

David Bundle
Jean-Robert Brisson
Immunochemistry Section
Division of Biological Sciences
National Research Council of Canada
Ottawa, Ontario CANADA K1A OR6

Professor Klaus Bock
Department of Chemistry
Technical University of Denmark
Lyngby, DENMARK

Canada



Difference n.O.e. experiments were performed on the disaccharide glycoside (displayed without the hydroxyl group hydrogen atoms) dissolved in D_2O (40 mgs/mL) containing 10% (v/v) acetone-d_6. Experiments were conducted in a 5 mm selective probe at 300 K. A total of 800 transients were collected and Fourier transformed with an exponential line broadening factor of 0.5 Hz. A - off resonance spectrum, B - difference spectrum recorded with D_2O lock, C - difference experiment obtained using acetone-d_6 lock.

United States Department of Agriculture | Agricultural Research Service | North Atlantic Area Eastern Regional Research Center | 600 East Mermaid Lane Philadelphia, Pennsylvania 19118

April 3, 1986

Professor B. L. Shapiro
Department of Chemistry
Texas A&M Newsletter
College Station, TX 77843-3255

Dear Dr. Shapiro:

Title: A Rapid, Dependable and Safe Perfusion System for Long Term In Vivo NMR Studies OR "Sleep Tight"

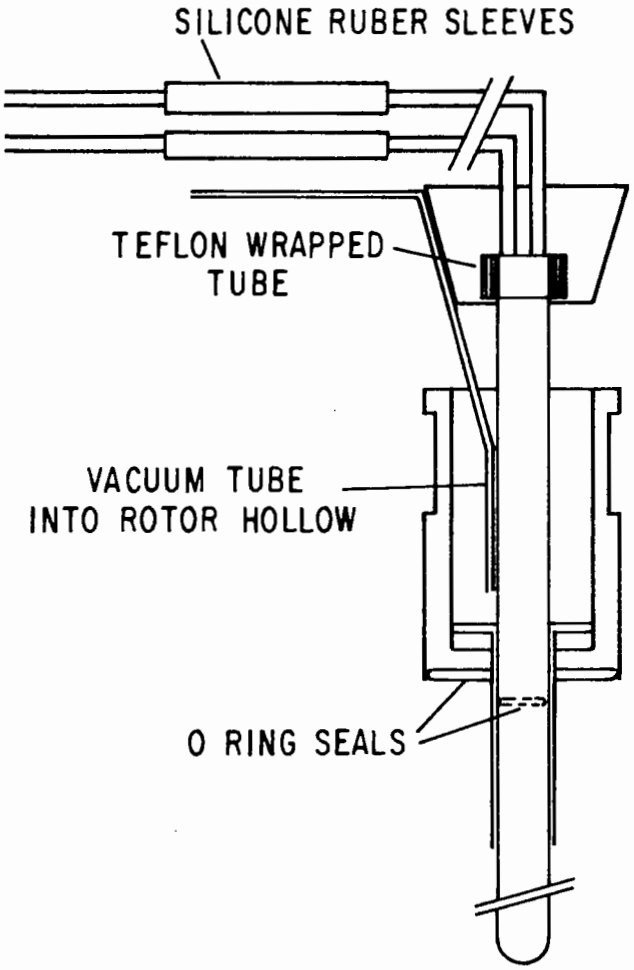
Because of the expanded use of in vivo NMR methods for examining stressed plant tissues over extended periods of time (up to 48 hours), we developed a need for a fail-safe perfusion system that would assure us of excellent flow stability and continuous high resolution homogeneity. By using the following circulating system for our in vivo ^{31}P studies of corn roots we are able to have comparatively restful nights while experiments of 45 hours plus are in progress.

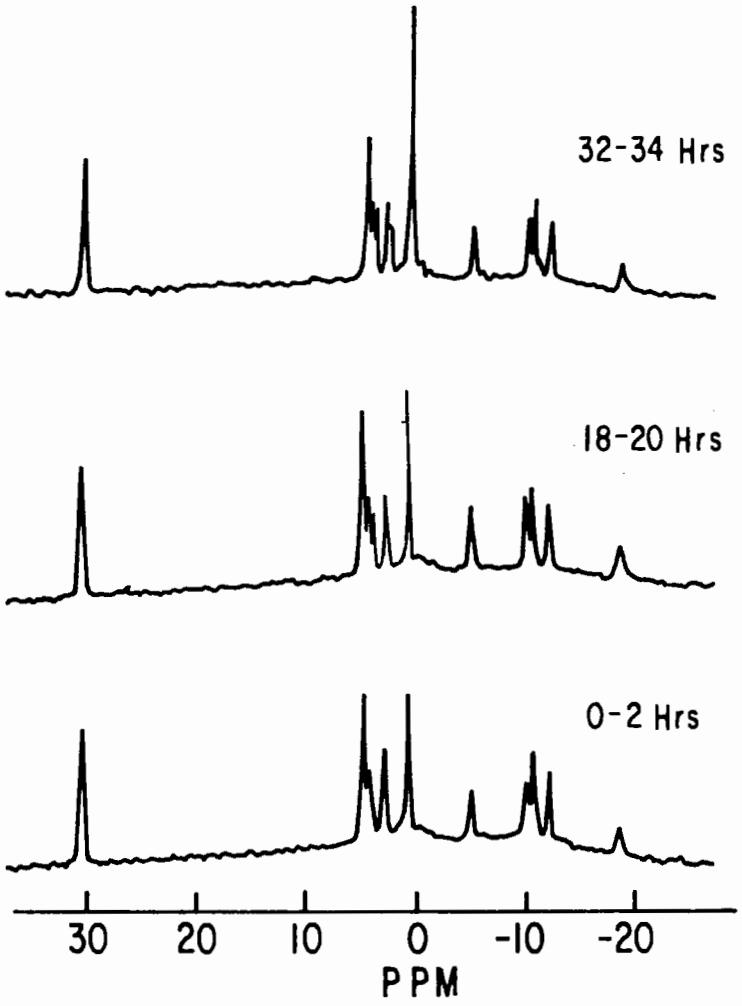
The system (Figure 1) does not use a vacuum in the actual movement of the perfusate (1), i.e., aerated nutrient solutions are pumped into the top of the tube and removed from the bottom below the roots (not shown), by a closed loop parastaltic pump (2). However, vacuum is used as one means of removing any possible leaked perfusate from the screw cap junction of the 10 mm NMR tube. A vee-shaped slit is cut into the rubber stopper to accommodate this additional tubing and allow the assembly to fit snuggly into the 54 mm magnet bore. Fortunately, the "safety" vacuum has rarely been needed.

The top of the ordinary 10 mm tube is wrapped with 1-1/2 mm of PTFE Teflon tape. This is screwed into a cap normally used for a threaded NMR tube, which by itself was found to be unsatisfactory. The cap is secured in a rubber stopper with epoxy resin glue. By using the Teflon wrap a virgin thread is cut each time, ensuring a perfect seal between cap and tube.

To add even more to our peace of mind, the inlet and outlet tubing from the reservoir has been cut and spliced with 2-inch lengths of silicone rubber tubing sleeves. In the event of a blockage, the sleeves will allow any pressure buildup to be released, a harmless six feet away from our valuable magnet.

The entire experiment can be run with a minimal amount of buffer (250 ml) and because no vacuum is needed for perfusate flow the buffer level is maintained in the tube without the problem of bubbles accumulating in the sample. Normally, any bubbles are removed prior to the start of an experiment and the positioning of the tube in the magnet.


SILICONE RUBER SLEEVES
TEFLON WRAPPED TUBE
VACUUM TUBE INTO ROTOR HOLLOW
O RING SEALS


32-34 Hrs
18-20 Hrs
0-2 Hrs
30
20
10
0
-10
-20
PPM

Previous perfusion designs have made use of either a complete flow-through system (3) which required a major modification of both probe and magnet cavity or a vacuum return loop design (1, 4) which limited experimental time to 30 minutes at 6-8 ml/min. because of the degradation of resolution due to the buildup of trapped air bubbles in between the tissue.

The system we have described has performed exceedingly well with no "expensive" mishaps since it was constructed 10 months ago. In general, our experiments can run from 20-48 hours while maintaining perfusion rates of 45-50 ml/min. without degradation of local field homogeneity. Figure 2 shows examples of ^{31}P spectra of corn roots taken at 2, 20 and 34 hours of continuous perfusion within our magnet.

RICHARD T. BOSWELL
Physical Science Technician
Plant and Soil Biophysics Research

PHILIP E. PFEFFER
Research Chemist
Plant and Soil Biophysics Research

2 Enclosures

(1) R. B. Lee and R. G. Ratcliffe, J. Exp. Bot. 34, 1213-1221 (1983).

(2) P. E. Pfeffer, S-I Tu, W. V. Gerasimowicz and J. R. Cavanaugh, Plant Physiol. 80, 77-84 (1986).

(3) J. K. M. Roberts, D. Wemmer, P. M. Ray and O. Jardetzky, Plant Physiol. 69, 1344-1347 (1982).

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Barry Shapiro
25 April 1986

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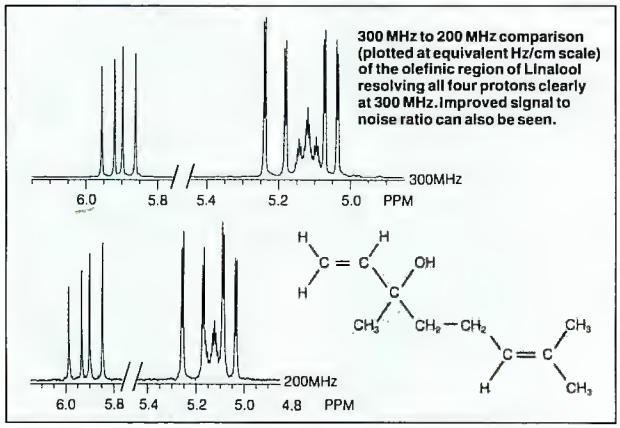

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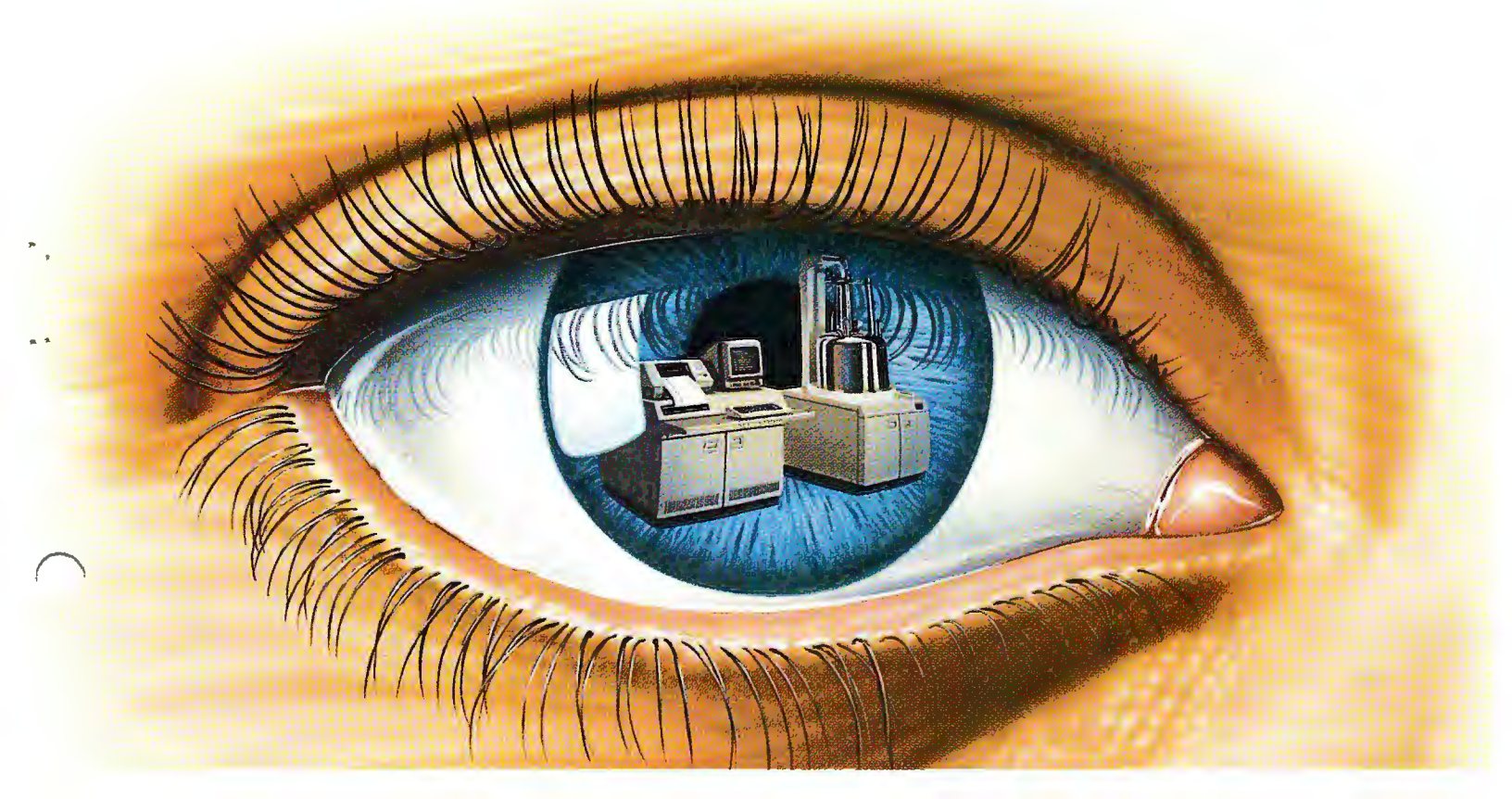

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April 4, 1986

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843-3255

RE: Quantitative Analysis of 2D NOE Experiments

Dear Professor Shapiro:

Recently we reported on our efforts to improve the quantitative analysis of the two-dimensional nuclear Overhauser effect (2D NOE) experiment (1,2). An important part of this work was the development of methods for correctly taking into account the magnetization transfer in complicated spin systems. Here, we report some additional data that we have obtained on an interesting experimental example of a multispin effect which was treated briefly in our original paper.(1)

In multispin systems the crosspeak volume between the resonances of two protons, "A" and "C", can be influenced by magnetization transfer through other neighboring protons. A simple example is a linear array of protons where magnetization can be transferred from proton "A" to "B" and finally to "C". An experimental example of a very similar case obtained from data on a glycopeptide antibiotic:peptide complex is shown in Figure 1. In this case the crosspeak between (G3,1') is due to direct magnetization transfer from G3 to 1' and also from magnetization transferred through G2 (i.e., G3 → G2 →1'). This additional mechanism for magnetization transfer from G3 to 1' can be determined from a full multispin analysis of the 2D NOE data. In Figure 1 our experimental crosspeak volume measurements (open circles) for the G3, 1' crosspeak are compared to a multispin simulation using the average relaxation rate matrix measured from the experimental data. The simulation (Figure 1A) displays a lag period in the initial part of the curve which is indicative of the presence of an additional indirect transfer of magnetization. The two magnetization transfer paths G3 → G2 → 1' (Figure 1B) and G3 → 1' (Figure 1C) are isolated in the simulations by zeroing the appropriate relaxation rates.

Experimental verification of the importance of the transfer of magnetization through G2 is shown in Figure 2. A series of 2D NOE experiments was recorded with selective saturation of proton G2 during the recycle delay and the mixing time (2A). This effectively cancels any indirect magnetization transfer through G2 in the 2D experiment leaving only direct transfer from G3 to 1'. In Figure 2B, slices from the normal 2D NOE experiment are shown. Spectra were scaled so that the intensity of the G3 resonance was the same in Figures 2A and 2B. The filled circles in Figure 1C correspond to the volumes measured from the experimental data shown in Figure 2A.

From this sort of analysis we are able to obtain more accurate distance constraints from our NOE data, leading to better structural information. Since this type of analysis requires many accurate volume integrations which can be quite time-consuming to obtain, software to facilitate 2D data analysis has been written.

Sincerely yours,

Edward Olejniczak

Steve Fesik

Robert Gampe

Erik Zuiderweg

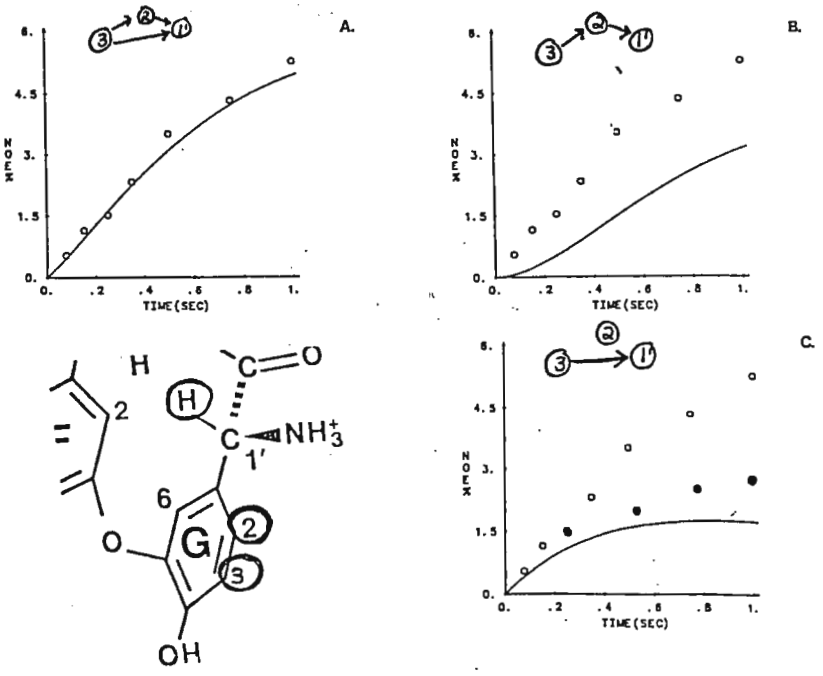
EO:SF:RG:EZ/jd

REFERENCES

(1) E. Olejniczak, R. Gampe and S. Fesik. J. Magn. Reson. (1986).

(2) S. Fesik, R. Gampe, T.J. O'Donnell and E. Olejniczak. J. Am. Chem. Soc. in press (1986).

Figure 1



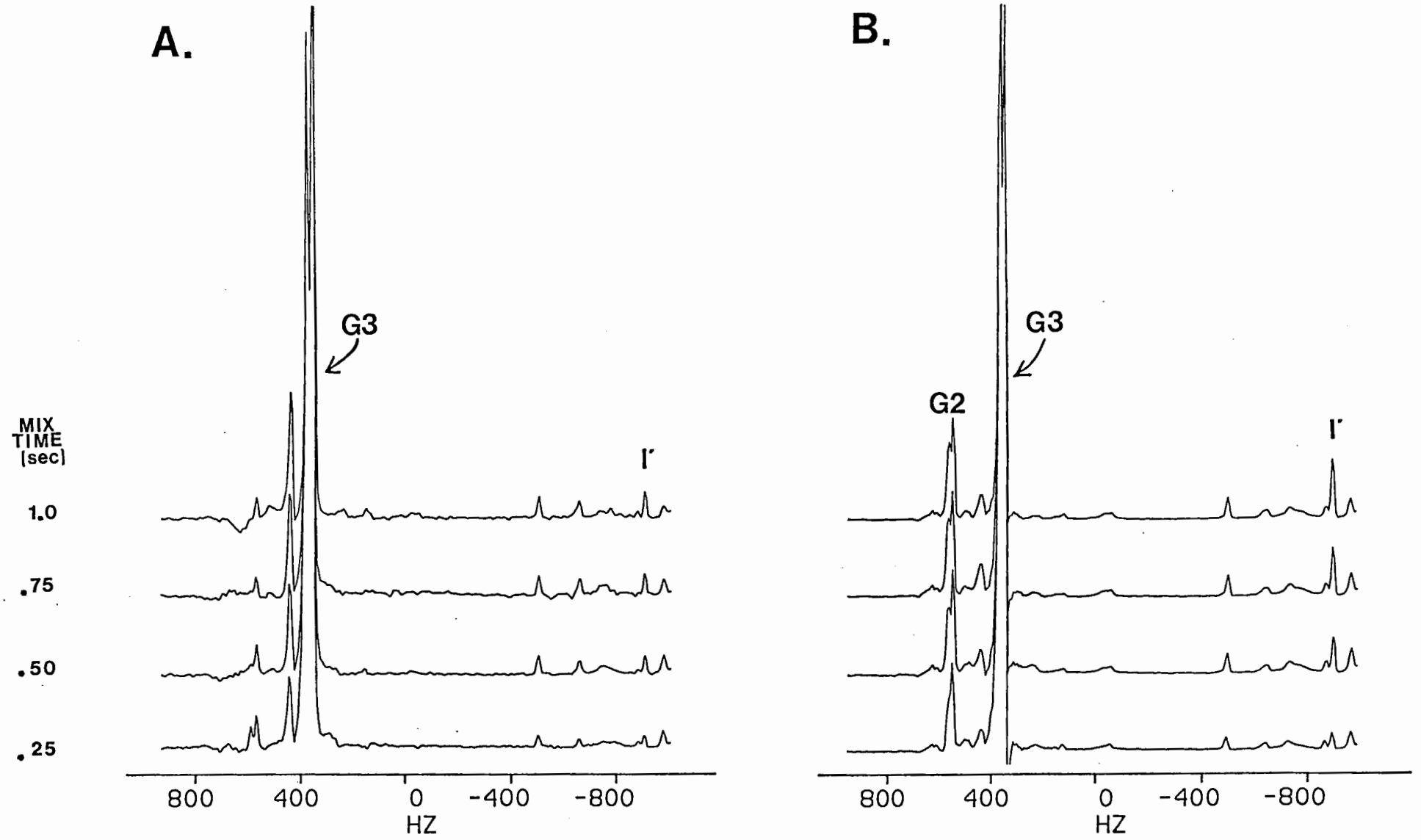


Figure 2

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Laboratorium für anorg. Chemie
Prof. Dr. L.M. Venanzi

Universitätstrasse 6
Telefon Durchwahl-Nr. 01/256 28 51
Telefonzentrale 01/256 22 11

Postadresse:
Laboratorium für anorg. Chemie
ETH-Zentrum
CH-8092 Zürich

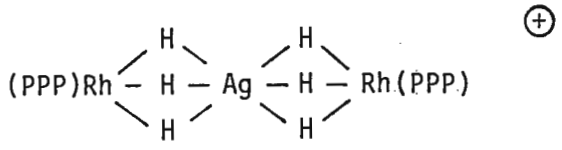
March 25, 1986

0410.05

Prof. Bernard L. SHAPIRO
Texas A&M University
Department of Chemistry
COLLEGE STATION, Texas 77843-3255
USA

Dear Professor Shapiro,

The chemistry of small clusters of transition metals has long attracted a great deal of attention. When the ligand atoms and metals are both NMR active these provide a wealth of coupling constant information. We have recently prepared some novel small clusters containing rhodium and silver with tertiary phosphine and bridging hydride ligands, one example of which is shown below, along with its ^{1}H spectrum in the hydride region. Using straightforward decoupling methods one can extract $^{1}J(^{107,109}Ag,^{1}H)$, ca. 60 Hz, a relatively rare coupling constant. We hope to learn even more from slowly emerging ^{107}Ag INEPT measurements.



PPP = $CH_3C(CH_2PPh_3)_3$

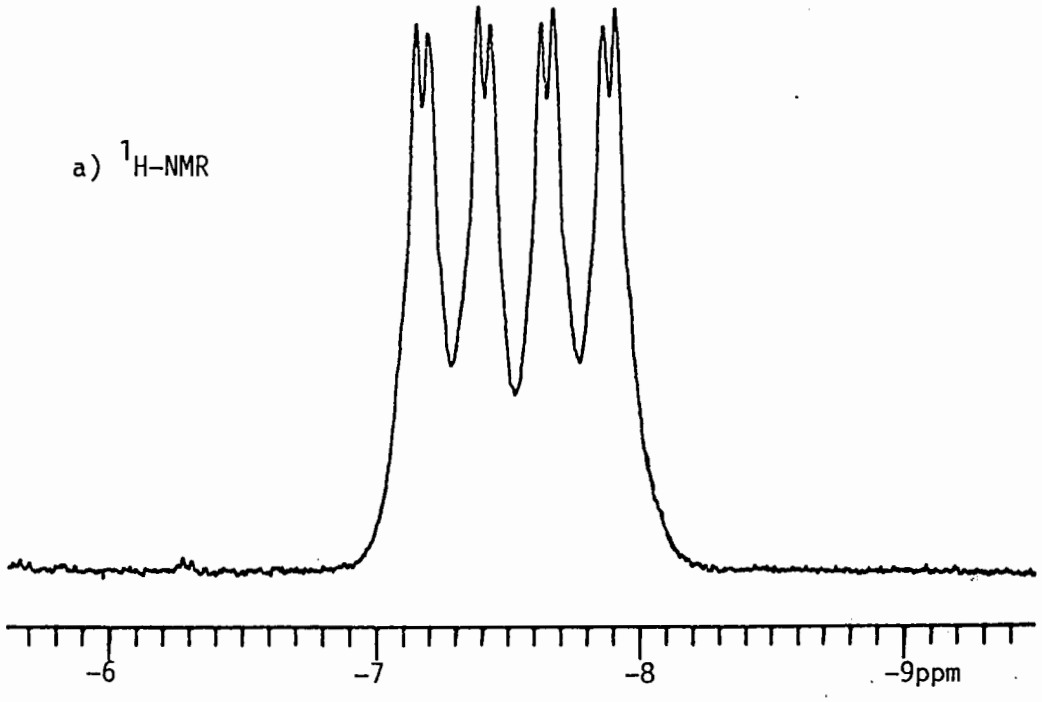
Yours sincerely

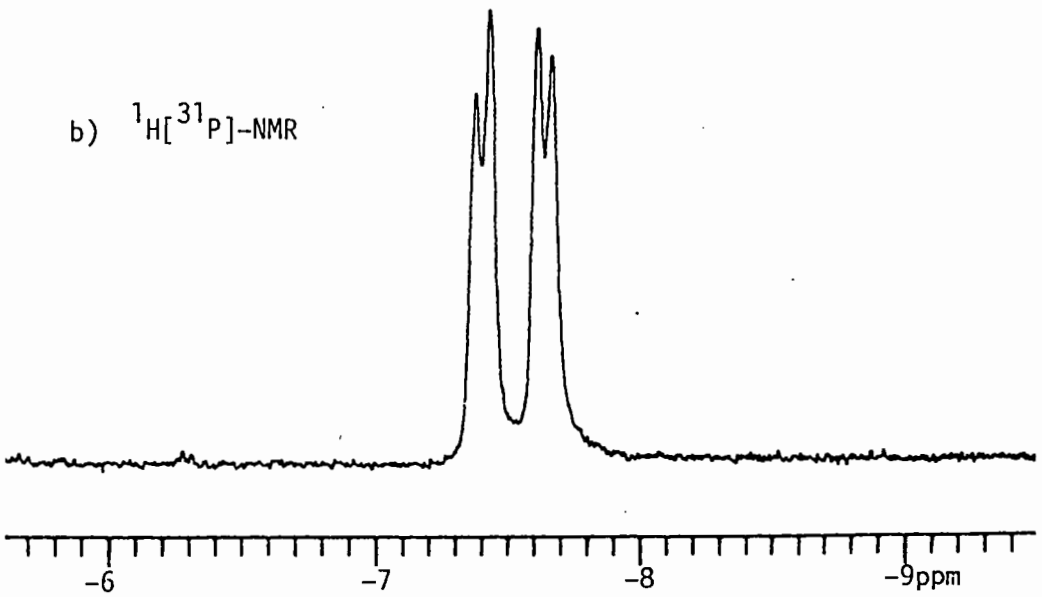
Luigi Venanzi

Suggested Title: $^{1}J(^{107}Ag,^{1}H)$ in a novel complex.

250MHz - ^{1}H-NMR-Spektrum von $[Rh_2Ag(\mu H)_6(PPP)_2]^+$

Hydridteil, gemessen in CD_2Cl_2 bei - 20°C





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March 26, 1986

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

OPEN ARCHITECTURES IN NMR SPECTROMETERS

Dear Professor Shapiro:

If you were to open a current issue of any micro or personal computer magazine you would find numerous references to the concept of an *open architecture*. One would say that a controversy was raging except for the fact that there appear to be no opponents.

An open architecture is an attribute of a computer whereby its manufacturer provides the user with detailed information about what's inside the computer. The purpose of this is not to awe the proud owner of the computer with how many horsepower there are under the hood but to give that owner the opportunity to make the most of it. Explaining how the computer is constructed enables other people to realize their ideas for improved and enhanced accessories by giving them the blueprints to incorporate and interface their designs. In favorable cases, this creates an atmosphere where a popular computer spawns a series of useful accessories by a variety of manufacturers and in turn, enhances the utility and popularity of the computer and the accessories and so on. This not only has the positive effects of providing a wide selection of new functions and improved performance from traditional functions but also helps to keep costs down through competition.

We face a similar situation in NMR spectroscopy. All commercial NMR spectrometers are built around proprietary architectures. We, as a community, must wait for the instrument manufacturers to provide us with new accessories, interfaces and features. This situation is changing, however, as several commercial systems have been developed around the Digital Equipment Corporation Q-bus architecture. This represents a definite positive step since the Q-bus represents an open, modular, building-block approach that is quite mature, having been around

for almost two decades. A plethora of products (including CPUs, memories, disk and tape storage, graphics display, printers, plotters and communications devices) is available from DEC and numerous third party vendors. Additionally, with the introduction of the μVAX II an unprecedented amount of computing power is now available at quite an affordable price. It is in this direction that I truly see our best opportunities for the next generation of NMR spectrometers.

Please credit this to Dr. Peter Jeffs' account.

Sincerely,

Joseph A. DiVerdi, Ph.D.
Associate Senior Investigator

UNIVERSITY OF CALIFORNIA, DAVIS

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UCD NMR FACILITY

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Post-Doctoral Position

Dear Professor Shapiro:

The University of California, Davis NMR Facility has an opening for a post-doctoral researcher as part of our NIH Regional Resource for In-Vivo NMR. The successful applicant should have (or be obtaining shortly) a Ph.D. in NMR spectroscopy with in-vivo/biological applications. He/she will participate in our core research program utilizing spatially selective in-vivo NMR techniques on a variety of nuclei as well as proton imaging. The UCD NMR Facility has available GE/Nicolet spectrometers with vertical magnets at 4.7, 8.5, and 11.8T; and a horizontal magnet 1.9T/310mm system. We are also currently negotiating the purchase of a 7T/175mm horizontal magnet spectrometer system for in-vivo spectroscopy and imaging. Those interested in applying for this position should write to Professor E. Morton Bradbury at the above address with inclusion of their CV and also provide two letters of recommedation. Starting date can be as soon as July 1, 1986.

Sincerely,

E. Morton Bradbury, Professor
Principal Investigator

Jeffrey S. de Ropp
UCD NMR Facility

The Binding of the N-terminal Peptide of Histone H4 to DNA involves Histidine Phosphate Interactions

Michael J. Minch,* Hieu Duc Pham and Dan Conners
Department of Chemistry, University of the Pacific, Stockton, Cal.
E. Morton Bradbury, J. S. de Ropp and G. Schroth
Department of Biological Chemistry, School of Medicine, UC Davis, Davis, Cal

All the structural changes in the eukaryotic chromosome as it condenses during mitosis and opens up again during the functional processes in the cell cycle involve changes in the interaction between DNA and chromosomal proteins, especially histones. Histones are highly basic proteins found with DNA in all eukaryotes in a complex known as a nucleosome, the simplest structural element of chromatin. Nucleosomal DNA is tightly wrapped around a histone octamer "core" containing two molecules each of H2A, H2B, H4 and H3 type histones. The core histones have one feature in common: at moderate ionic strengths the central and C-terminal regions of the histones adopt globular protein structures that self complex whereas the N-terminal regions are very rich in cationic amino acids and remain in a random coil under such conditions. The N-terminal regions of core histones are not involved in maintaining histone globular structure or in stabilizing histone-histone interactions within a core particle but this region must play some significant role in chromatin organization. The facts that the N-terminal amino acid sequences of H3 and H4 are rigidly conserved and that acetylation of four lysines in the H4 N-terminal region is coordinated with changes in chromatin organization makes no sense otherwise! **The role of the N-terminal regions remains an enigma.**

For this reason we have been examining the DNA binding ability of the 23 amino acid N-terminal peptide fragment H4(1-23) released by aspartate cleavage of H4, in order to probe the role of specific amino acid residues in the binding mechanism. At 500 MHz good quality spectra of 1.6 mM H4(1-23) can be obtained. The spectra exhibit sharp resonances typical of random coil peptides over the temperature range 5° to 26° indicating little or no tendency to adopt secondary or tertiary structure in aqueous solution. Because of the somewhat redundant amino acid composition of this peptide (e.g. 8 Gly and 4 lys), assignment of all resonances to specific amino acids is not possible for the resonances which overlap entirely but all non-overlapping resonances have been assigned, based on chemical shifts, spin multiplicities, and two-dimensional J correlated spectroscopy (COSY).

The ^1H assignments given in Table I are based on these methods. High field NMR in 90% H_2O by the 1331 water suppression pulse sequence indicates rapid exchange of backbone amide protons, confirming the absence of significant secondary or tertiary structure. Natural abundance ^{13}C spectra of the peptide at two different pH-values feature chemical shifts and overlapping resonances characteristic of random coil peptides.

Table I
^1H Chemical Shifts for H4(1-23) Peptide

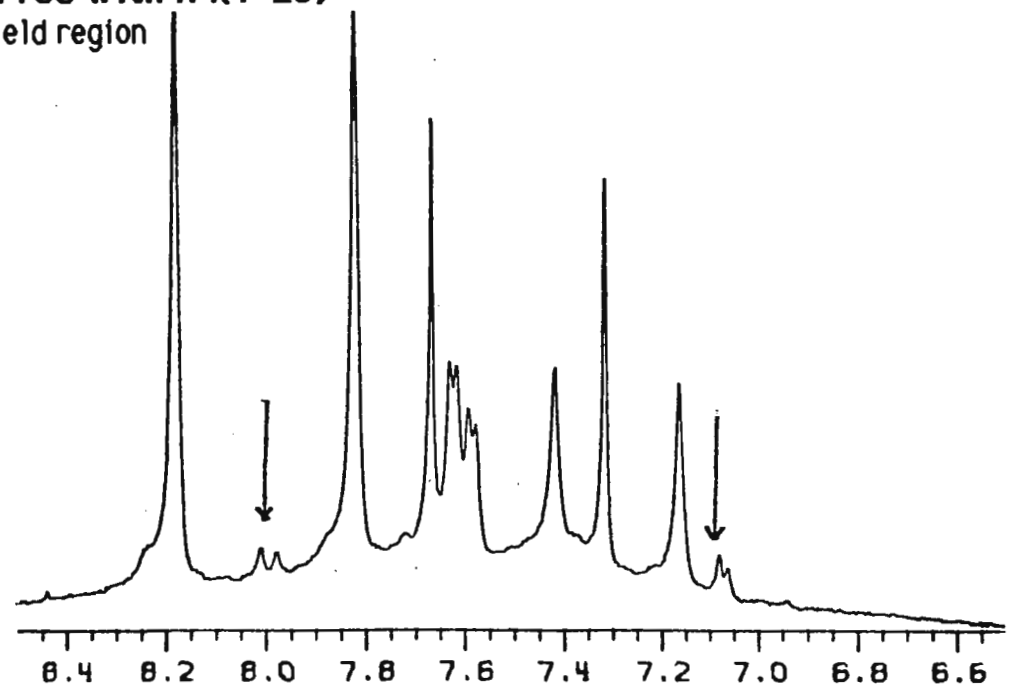
δ-value, ppm	Residue	δ-value, ppm	Residue
0.85, 0.92	leu δ-CH_3	0.92	val γ-CH_3
1.38	ala β-CH_3	1.4-1.5	lys γ-CH_2
1.55	arg γ-CH_2	1.6	leu γ-CH_2
1.6-1.8	lys β,γ-CH_2, arg γ-CH_2	1.87	arg β-CH_2
1.95	lys acetyl	2.04	val β-CH
2.07	ser acetyl	2.87	lys N-methyl
2.99	lys ε-CH_2	3.12	Ac-lys ε-CH_2
3.18	arg δ-CH_2, his β-CH_2	3.87	Ac-ser β-CH_2
3.93	gly α-CH_2	3.9	ser β-CH_2
4.07	val α-CH	4.16	ser α-CH

Interestingly we found that the ^1H spectrum of the peracetylated peptide does not indicate any significant change from the random coil conformation.

In addition to the residues given above, the H4(1-23) peptide contains a histidine residue with characteristic C(2) and C(4) imidazole ring protons. The pK_a of the single histidine residue (6.8)was determined from ^1H spectra in D_2O as a function of pH (2.07 to 9.70); the C(2) and C(4) proton resonances move downfield >0.5 ppm when the histidine becomes fully protonated.

500 MHz ^{1}H spectra of H4(1-23) with various concentrations of natural and synthetic oligonucleotides indicate that the binding profoundly shifts the histidine C(2) and C(4) proton resonances downfield and increases the pK_a of this amino acid residue, implying strong electrostatic stabilization of the protonated residue when associated with the oligonucleotide backbone. With 200-300 BP DNA, the peptide glycine α-CH, lysine N-CH_2 and N-CH_3 and arginine N-CH_2 resonances broaden preferentially indicating a number of H-bond associations in addition to electrostatic interactions but the most conspicuous change in the histidine ring protons. Moreover the histidine C(2) and C(4) proton signals each appear as two peaks separated by 60 Hz suggesting a slow exchange betwen two conformational forms, probably involving the orientation of the histidine side chain when bound to the phosphate backbone. Much the same results have been observed for H4(1-23) with various concentrations of low molecular weight oligonucleotides [GGAATTCC (see below) and CGCGAATTCGCG] where the lines are not as broad and the "splitting" of the histidine resonances is more apparent. To date variable temperature studies (5° to 55°) have not led to a coalescence of the double peaks; at substantially higher temperatures peptide binding is precluded. Analysis of this very interesting phenomenon awaits additional data including ^{13}C studies. The amino acid sequence about the histidine is quite unusual (lys-arg-his-arg-(me)lys) and may permit a stable "chelate" structure of cationic side chains organized about the oligonucleotide phosphorus.

GGAATTCC with H4(1-23)
downfield region



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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue, Argonne, Illinois 60439

March 19, 1986

Prof. Bernard Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843-3255

RE: Solid ^{13}C NMR of Clay/Organic Complexes with Off-Line Data Processing

Dear Barry:

Recently, we have become interested in applying solid ^{13}C NMR to study intermolecular interactions between two organic compounds - methyl green (MG) and bioresmethrin (BR), a powerful contact insecticide - adsorbed on montmorillinite clay, and their separate interactions with the clay surface. Despite its effectiveness against a wide range of insect pests and its being one of the safest pesticides (acute oral LD_{50} for rats is 8g/kg), bioresmethin is of limited use in agriculture owing to its rapid photodecomposition. Earlier studies (Margulies et al., Nature) have demonstrated a stabilization of BR toward photodegradation by adsorbing it on montmorillinite clay together with the divalent cation methyl green. In addition, FTIR results implied that the stabilization effect is due to specific interactions between the two compounds at the surface of the clay.

The ^{13}C CP/MAS spectrum (a) of crystalline BR taken on our Bruker CXP spectrometer operating at 25.18 MHz for ^{13}C at a spinning rate of 4.1 KHz is shown in Figure 1. The resolution is seen to be excellent and resonance lines apart from the individual methyl carbons can be assigned unambiguously with the aid of an interrupted decoupling spectrum (b), using a delay time of 100 μs, and by comparing carbon shifts in the solid ^{13}C spectrum (c) of benzylfurylmethanol.

Some details of the interactions of the two compounds at the molecular level can be obtained from CP/MAS data shown in Figure 2. A comparison of spectrum a (0.4 mmol/g BR adsorbed on clay) with spectrum b (0.2 mmol/g BR adsorbed on clay in the presence of MG) reveals the disappearance of C1, C2, C3 and C5 resonances of BR with a concomitant appearance of new resonances to higher field. (Note: MG adsorbed on clay gives no observable NMR spectrum under the same conditions). These changes, although at present difficult to interpret with regard to the chemical nature of the interaction, imply a specific involvement of the furan moiety in BR. Studies are now in progress on structurally less complicated systems in an attempt to unravel the nature of these interactions.

Finally, we are now able to transfer NMR spectra or FID's from our Aspect 3000 computer to the Chemistry Division's VAX 11/780 computer for subsequent data manipulation and/or enhanced graphics capabilities. For example, the figures presented here were generated on our group's HP7550A plotter. The transformed spectra were converted to ASCII files using a Pascal routine developed in house and subsequently transferred from the Aspect 3000 to the VAX. Data points representing the imaginary part of the spectrum were discarded, and the real points assembled into a format suitable for plotting using TELLAGRAF computer graphics.

Sincerely,

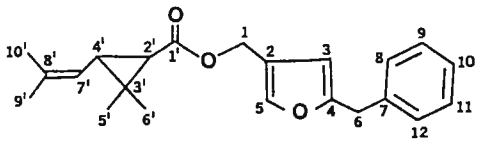
Robert E. Botto
Chemistry Division

Paul Neill
Chemistry Division

L Ruzo
Luis O. Ruzo
Univ. of California
at Berkeley

L Margulies
Leon Margulies
The Hebrew University
of Jerusalem

Figure 1.



(BR)

a
8,9,11,12
10
7'
2
3
1
6,2',4'
3'
9',10'
5',6'
1'
4
5
7
8'
b
1'
4
7
8'
2
3'
CH3's
c
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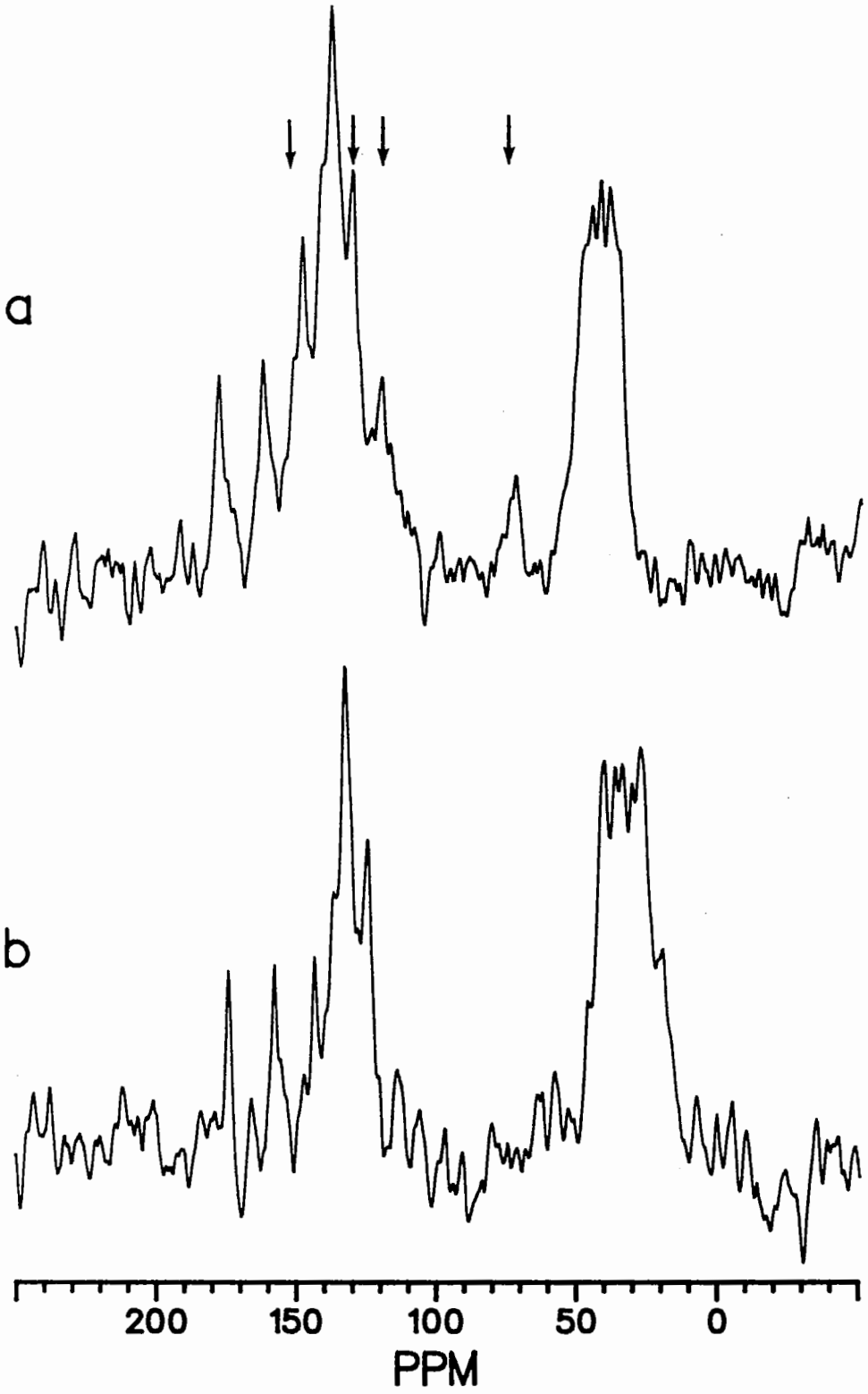
150
100
50
0
PPM

Figure 2.



UNIVERSITY OF MINNESOTA
TWIN CITIES

College of Forestry
Department of Forest Products
Kaufert Laboratory
2004 Folwell Avenue
St. Paul, Minnesota 55108

March 28, 1986

Dr. B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843-3255

NMR of Kraft Lignins

In nature lignin is the second most abundant macromolecule after cellulose, but due to its complexity and physical properties its macromolecular structure is still poorly understood. Our studies of kraft lignins (byproduct lignins from sulfate pulping) are devoted to understanding the structure and physical properties of native lignin as well as the structural modifications that occur in the kraft process.

We have spent a great deal of time learning to prepare paucidisperse fractions from the parent molecular weight distribution typified by Figure 1. The problems encountered in our isolation and purification are actually quite profound. Figure 2 shows two proton NMR spectra which exemplify the molecular weight dependence of the aromatic and aliphatic hydroxyl group functionality. The proton and the carbon-13 spectra exhibit rather discouragingly broad envelopes of peaks, even though the samples have been carefully fractionated according to molecular weight. The broad envelopes of peaks are not due to a diversity of molecular species, but rather arise from the complexation and organization of the molecules in solution which leads to very efficient relaxation. This initial proton and carbon-13 study will afford the first coherent data on the variation in lignin functionality with molecular weight; indeed these changes suggest that the higher molecular weight species are little changed from the native macromolecular structure. Now that we can produce well defined lignin samples, we are able to plan appropriate relaxation and NOE studies and anticipate effects arising from the structure, associative properties and macromolecular dynamics of the components in solution. Additionally, we have some hope of obtaining well resolved NMR spectra of high molecular weight lignin components since chromatographic and spectroscopic evidence indicates that there is structural regularity in lignin.

Please credit this letter to the account of Steve Philson, University of Minnesota Chemistry Department.

Sincerely,

Ted Garver

Ted Garver

Simo Sarkanen

Simo Sarkanen

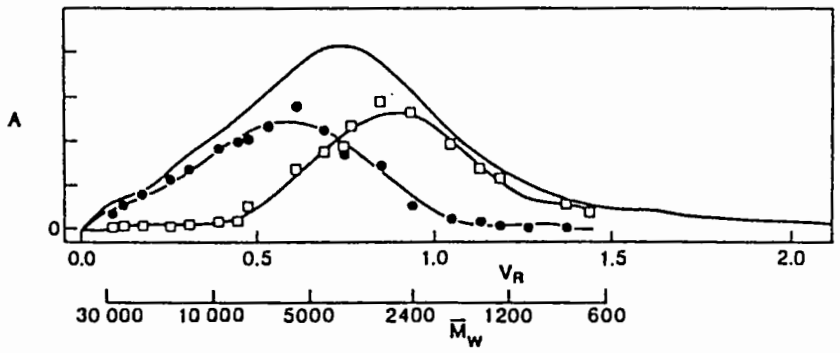


Figure 1. Molecular weight distribution of dissociated kraft lignin showing component subsets created by adsorption chromatography of fractions.

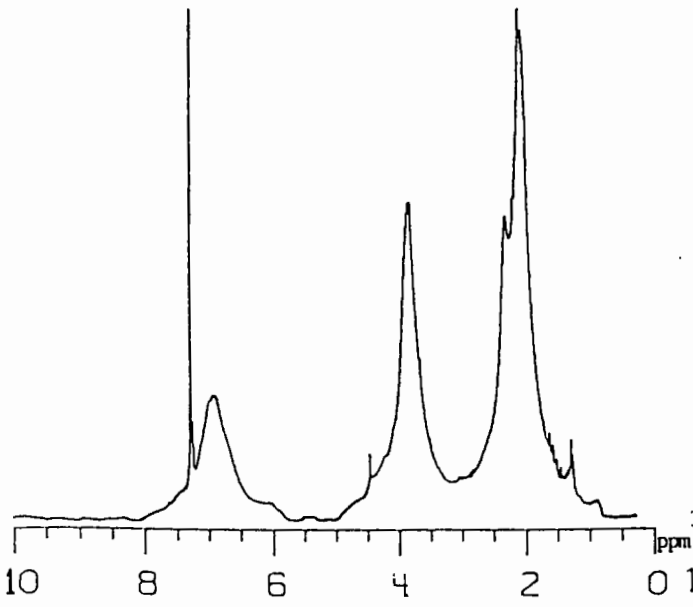


Figure 2a. Proton NMR of acetylated paucidisperse kraft lignin fraction with molecular weight 9000.

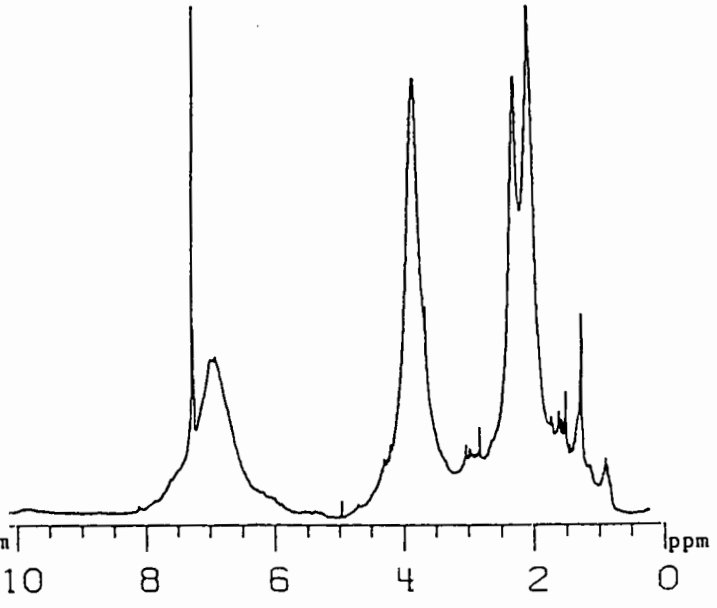


Figure 2b. Proton NMR of acetylated paucidisperse kraft lignin fraction with molecular weight 2900.

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

onderwerp Flow measurements with NMR

Dear Professor Shapiro,

By making use of a repetitive pulse sequence in combination with a magnetic field gradient in the direction of flow (RP method) it is possible to measure the flow velocity of fluids in a variety of conducting elements (e.g. glass capillaries,plant xylem vessels,veins and arteries) (1,2).
Fig. 1a represents 2 typical signal response curves for the flow experiments.From these curves we obtain the following information:

1.Linear flow velocity($\bar{v}$ in mm/s);its value is directly proportional to the reciprocal of the time at which the maximum of the signal occurs(t_{max})(Fig.2) (1).
2.Volume flow velocity(Q in mm^3/s);its value is directly proportional to the initial slope $dS/dt)_{t=0}$ (Fig.3) (3).
3.The effective cross-sectional area for flow(A);$A=Q/\bar{v}$.

This is illustrated in Fig.1a+b.In Fig. 1b the sample in which flow is measured,is shown.The region 1 contains 50 capillaries(0.278 mm diameter).Flow-curve 1 in Fig.1a originates from this region.Region 2 in Fig. 1b is a tube with a 2.3 mm radius.Curve 2 in Fig. 1a is a recording of the NMR signal of this region.During the measurements of curves 1 and 2 in Fig. 1a the volume flow rate was identical.Indeed,the initial slopes of curves 1 and 2 are identical.
The total cross-sectional area of the regions 1 and 2 has a ratio 1.4;this should also be the ratio of $1/t_{max}$ of curves 1 and 2 in Fig. 1a.Within experimental error this figure is indeed obtained.

(1) M.A.Hemminga,P.A.de Jager,J.Magn.Res. 37,1(1980)
(2) H.van As,T.J.Schaafsma,Biophys.J. 45,469(1984)
(3) H.van As,T.J.Schaafsma,manuscript in preparation.

Please put this contribution on my account(TJS).
Also on behalf of J.E.A.Reinders and H. van As,

Sincerely,
Schaafsma
(T.J.Schaafsma)

Fig. 1a.

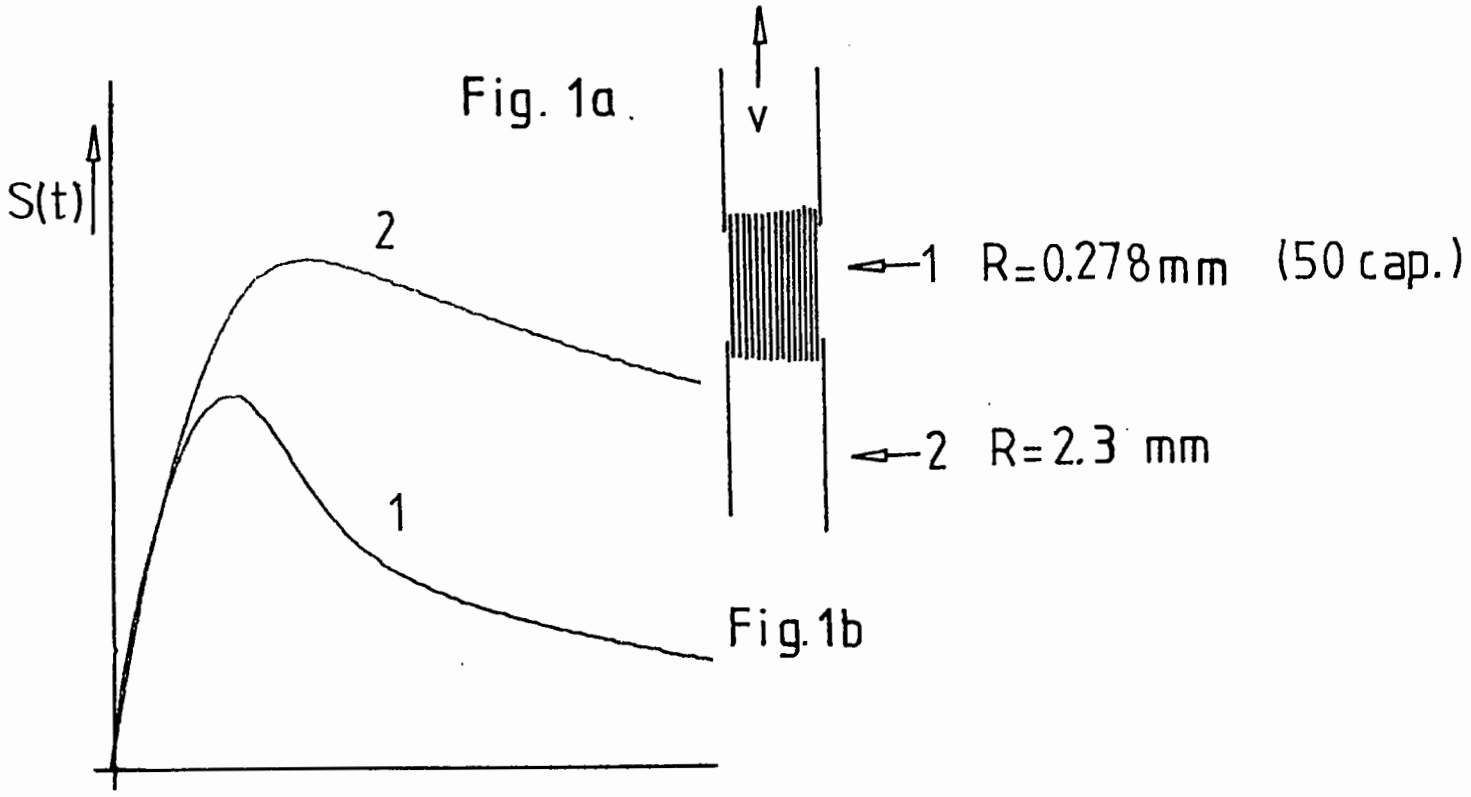

Fig. 1b

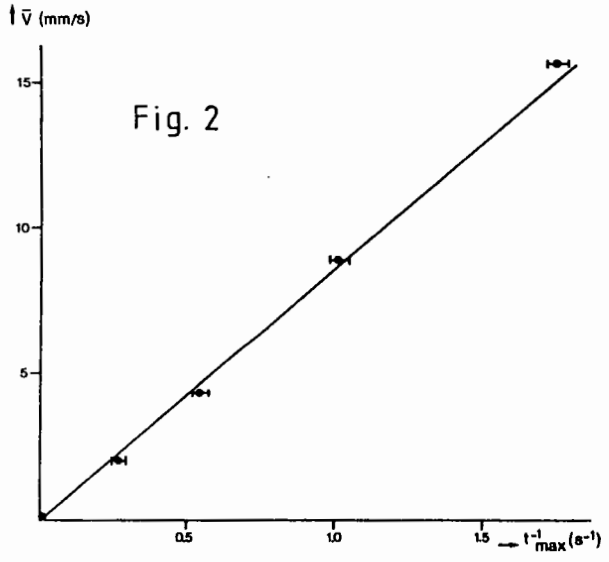

Fig. 2

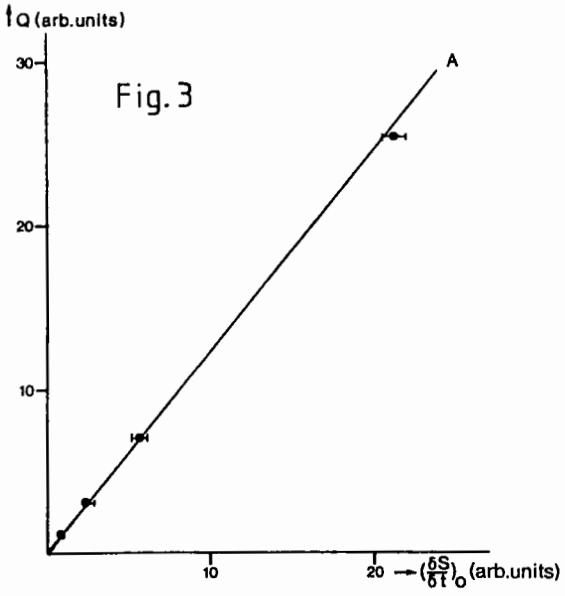

Fig. 3

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

Your reference and date	Our reference	Office telephone	Date
	91/86/JC/mvdg	015-781022	1 April 1986

Subject
A simple device for respiration synchronization in magnetic resonance imaging

Sub-division

Dear Professor Shapiro,

The artefacts due to motion in magnetic resonance Fourier imaging of live animals and humans are well known nowadays; they consist of a modulation or blurring of the images in the phase encoding direction. Several solutions of different type have been proposed in the literature (1).

The purpose of this contribution is to describe a simple device for respiration synchronization which we use in the imaging of the moving liver of live rats.

The respiration of the animal is sensored by means of a small plastic bellow (meant for taking blood pressure from babies) inflated with air (10 cm H_2O) and coupled with a pneumatic line to an U-shaped tube containing alcohol.
The breathing of the animal changes the pressure of the air in the bellow which in turn alters the level of the liquid in the U-shaped tube. This level is being monitored by means of a capacitive sensor (2) and a triggering circuit allows for deriving a triggering pulse from the obtained respiration signal.
For each successive value of the phase encoding gradient, the pulse programmer which controls the timing of the complete imaging procedure is instructed to wait for the trigger pulse from the respiratory device, which effectively synchronizes the experiment with respiration. A variable delay time enables one to observe the NMR signal in any phase of the respiratory cycle at will.

We want to remark that pneumatic sensoring of the respiration is attractive since no electric conductors have to be introduced into the RF probe (decoupling problems, RF field disturbances)

while the capacitive sensor converts the pressure variations into a breathing signal with a high signal to noise ratio. Thus an effective device for respiration synchronization has been developed.

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(1) RL Ehman et al., Am.J.Roentg. 143, Dec. 1984, 1175-1182
(2) WChr. Heerens, J.Phys.E: Sci.Instrum. 15, 1982, 137-141

Yours sincerely,

M.A. Moerland D. Korbée J.H.N. Creyghton W.M.M.J. Bovée

Montana State University
Bozeman, Montana 59717

Department of Chemistry
College of Letters and Science

Telephone (406) 994-4801

March 31, 1986

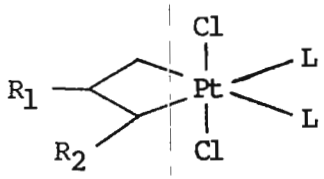
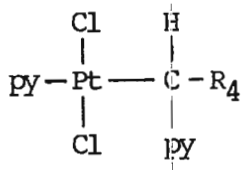
Platinum-195 Chemical Shifts

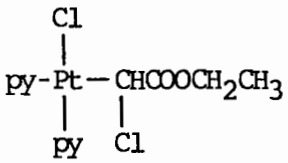
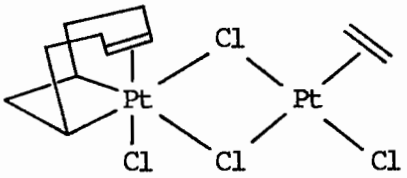
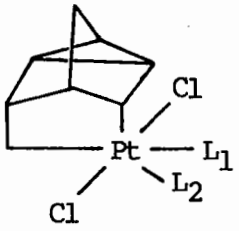
Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843

Dear Barry,

^{195}Pt NMR is a valuable structural probe for organometallic and coordination chemists and its observation is routine in many institutions. While several empirical rules[1] have been developed to assist the experimentalist in predicting chemical shifts for this nucleus, holes remain in the data base.

The following table lists data collected over several years on a variety of organoplatinum complexes. All of this data was collected on a Brucker WM 250 NMR operating at 53.655 MHz. Numbers reported are downfield from a standard 1.0 M $Na_2Pt(CN)_4$ in D_2O solution at 20 C. We prefer to use the tetra-cyanide as a standard rather than the more commonly used $PtCl_6^{-2}$ ion. The $Pt(CN)_4^{-2}$ ion is less affected by temperature (less than half as much as the hexa-chloro), and is at higher field than most other Pt complexes. This permits shifts to be reported as positive values. Finally, it is less sensitive to solvent effects (see below). All data was taken at 20 C, unless otherwise indicated. # Examples means the number of examples of this type of structure that we have observed. In the cases where structural types are given rather than a specific compound, the range of the Pt shifts are given.

STRUCTURE	# EXAMPLES	SOLVENT	PPM
$Na_2Pt(CN)_4$		D_2O DMSO	0.0 40.4
Na_2PtCl_6		D_2O DMSO	4736 ~4336[1]
	15	$CDCl_3$ or THF	3263-[2] 3591
	5	$CDCl_3$	1817- 1890
$PtCl_2(py)$ (olefin)	4	$CDCl_3$	1778- 2107

STRUCTURE	L_1/L_2	SOLVENT	PPM
		$CDCl_3$ (trans isomer	1966 -1984)
$PtCl_2$ (CO) (ethylene)		$CDCl_3$	781
		$CDCl_3$	2796[3] 2107
	py/py	$CDCl_3$	2860[2]
	py/py	" (L.T.)	2842
	py/PO_3	" (L.T.)	2409
	PO_3/PO_3	" (L.T.)	2395

L = pyridine and tetrahydrofuran, py = pyridine, THF = tetrahydrofuran, PO_3 = triphenylphosphine, R_{1-3} are aliphatic while R_4 may be aliphatic or aromatic, (L.T.) = -30 C.

Sincerely,

Tim Hanks
Graduate Research Assistant

Edie Parsons
Graduate Research Assistant

1. P. S. Presgosin, Coord. Chem. Rev., (1982), 44, 247-291.

2. a) M. D. Waddington, P. W. Jennings, Organometallics, (1982), 1, 1370. b) M. D. Waddington, J. A. Campbell, P. W. Jennings, Organometallics, (1983), 2, 1269. c) R. A. Ekeland, P. W. Jennings, J. Organometallic Chem. (1985), 281, 397. d) M. D. Waddington, Ph.D. Thesis, Montana State University, 1983. e) R. A. Ekeland, Ph.D. Thesis, Montana State University, 1984.

3. E. J. Parsons, R. D. Larsen, P. W. Jennings, J. Am. Chem. Soc., (1985), 107, 1793.

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1986 April 03

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

DU PONT CANADA
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^{13}C CHEMICAL SHIFT MEASUREMENTS IN UREA ADDUCTS

Dear Barry:

The structure and motions of long chain molecules, trapped within the channel which is formed in a urea adduct, are of interest because they exist in a well defined environment for molecular motion. As part of an ongoing interest in the structures and motions of guest molecules we have been collecting ^{13}C CP/MAS spectra of these compounds in order to ascertain if the chemical shifts can be correlated with the well defined solid state structures which the guest molecules must adopt in the channel. Despite careful referencing using TMS and adamantane the data, which was acquired over several years at two different magnetic fields (2.1 and 4.7 T), showed a bewildering lack of consistency in itself and with other published chemical shift data. The recent realization[1] that ^{13}C chemical shifts exhibit a field dependence arising from a second order dipolar perturbation makes the inconsistencies in the data all fall into place.

Figure 1 shows the 50.3 MHz ^{13}C solid state CP/MAS spectra of neat stearic acid (A) and the stearic acid/urea adduct (B). The solid state resonances were referenced to internal adamantane and assigned by comparison with the spectra of selectively deuterated stearic acids (both as neat solids and as urea adducts). Comparison of the methylene chemical shifts for the neat solid stearic acid at 22.63 and 50.30 MHz showed that the latter data were shifted an average of 0.25 ppm to higher field, in good agreement with the 0.26 ppm chemical shift difference predicted for this magnetic field difference[1]. When the stearic acid was trapped in a urea channel the average chemical shift difference for the methylenes was only 0.05 ppm, close to the 0.04 ppm difference expected for an all-trans chain rotating rapidly about its long axis. This rapid rotation of the all-trans chain is found in urea adducts of linear molecules[2,3]. In fact, the average chemical shift difference for methylene units at 22.636 and 50.30 MHz, in 6 different linear molecules (a total of 23 different methylenes), is 0.26 ppm for the neat solids, but only 0.05 ppm for the corresponding adducts.

This high correlation with theory does not extend as well to aromatic and carbonyl carbons, principally because those resonances at 22.6 MHz are somewhat broader due to poor field homogeneity and a less precise setting of the magic angle.

While there are other more elegant methods for demonstrating that the guest molecules do indeed rotate inside urea channels, the ability to obtain accurate, carefully referenced chemical shifts is useful for

(continued on page 57)

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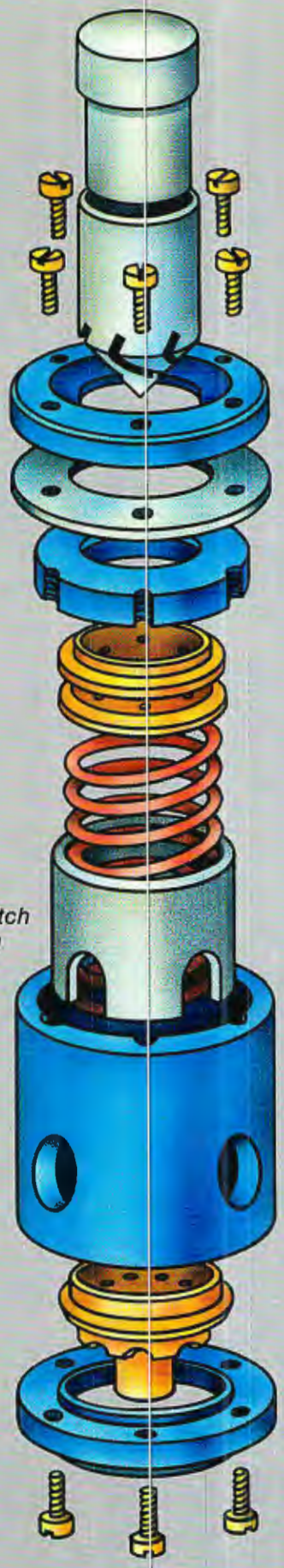

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M295C	12 gauss (5μsec)	4 KHz	2 KHz	only accepts Ceramic/KEL-F rotors
M275	20 gauss (3μsec)	10 KHz	5 KHz	fast spinning system, for non ^{13}C appl.
M275C	20 gauss (3μsec)	6 KHz	4 KHz	only accepts Ceramic/KEL-F rotors
M395	10 gauss (6μsec)	5.5 KHz	N/A	triple bearing system for wide bore
M375	15 gauss (4μsec)	8 KHz	N/A	flipper or VASS probes only

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295D	9.5mm	7.1mm	0.56ml	DELRIN®	5 KHz @ 20 psi	multinuclear, routine
295K	9.5mm	5.4mm	0.35ml	KEL-F®	3.8 KHz @ 15 psi	routine, no C13 background
295T	9.5mm	7.1mm	0.56ml	TORLON®	6 KHz @ 28 psi	multinuclear, dense materials
295C	9.5mm	7.9mm	0.78ml	CERAMIC	4 KHz @ 16 psi	highest sens., no C13 background
275T	7.5mm	3.6mm	0.13ml	TORLON®	10 KHz @ 40 psi	highest speed, Al, B and Si free
275T	7.5mm	4.5mm	0.21ml	TORLON®	8 KHz @ 35 psi	high speed, volume; Al, B, Si free
275C	7.5mm	6.0mm	0.45ml	CERAMIC	6 KHz @ 15 psi	highest speed, no C13 background
395D	9.5mm	7.1mm	0.56ml	DELRIN®	4 KHz @ 20 psi	highest stability, triple bearing
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(continued from page 54)

probing structural changes in the channel. Since stearic acids exist in the urea channel as a dimer and because of the spatial constraints imposed by the channel, the acid moieties and adjacent methylenes are strained and this is reflected in the solid state chemical shift changes observed in spectra A and B.

Yours sincerely,

Eric C. Kelusky

Eric C. Kelusky

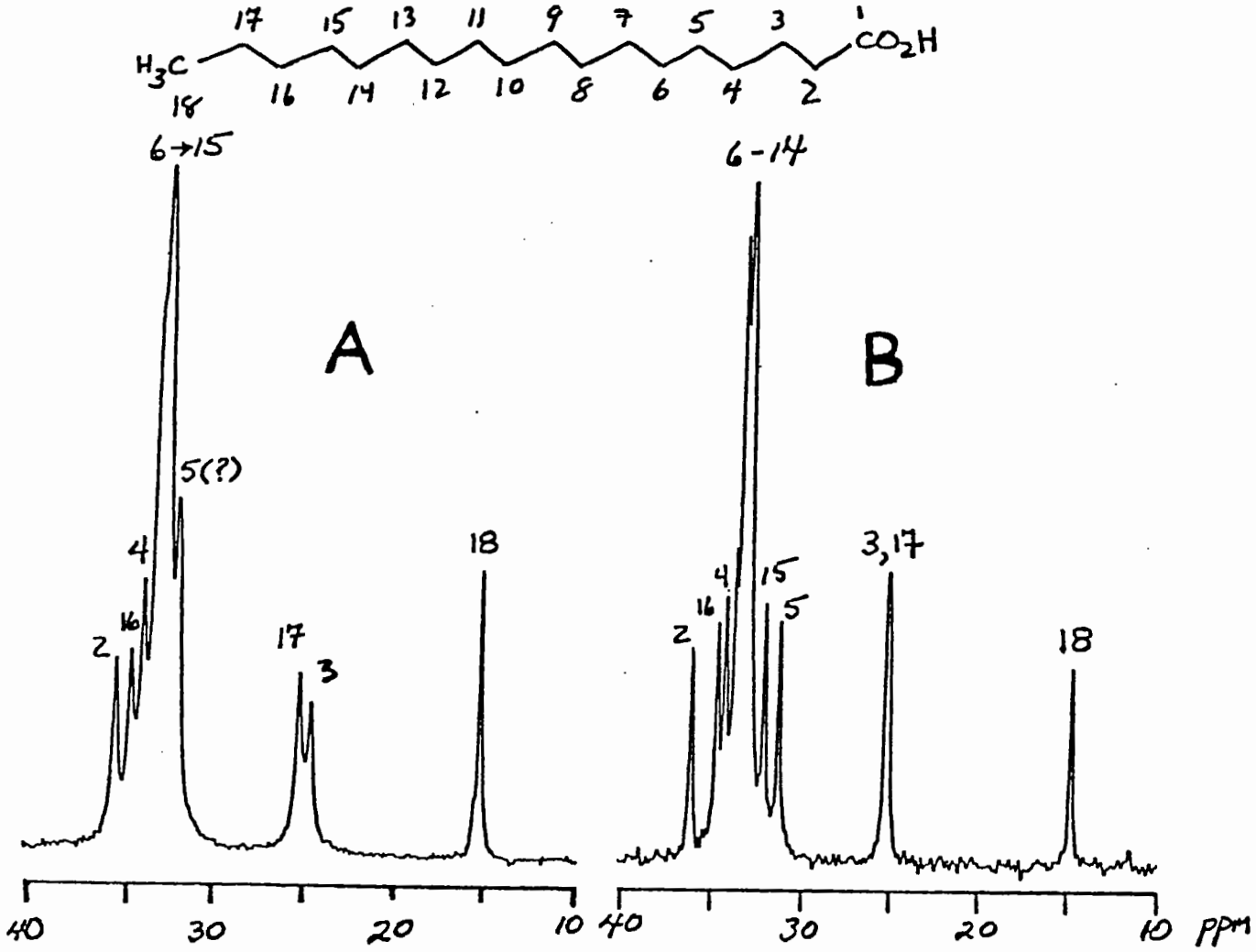

Figure 1. (A) ^{13}C CP/MAS spectrum of stearic acid acquired at 50 MHz with a 1 msec. contact time and an 8 second recycle time, spinning at 2 kHz .
(B) ^{13}C CP/MAS spectrum of the stearic acid/urea adduct, same conditions as A.

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2. H.L. Casal, D.G. Cameron and E.C. Kelusky, J. Chem. Phys., 80, 1407, 1984.
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Department of Chemistry

CLARK UNIVERSITY

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7 April 1986

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

Dear Barry:

Title: Spin-Diffusion using the DANTE sequence with ^{13}C CP/MAS

We have recently attempted to detect ^{13}C spin diffusion between different components in a solid polymer blend using selective excitation as described by Ernst et al (1). The pulse sequence is as shown:

^{1}H: $90^{\circ}_{\pm x}$, Decouple$_y$, τ_m, , Decouple

^{13}C: , CP_x, 90°_{-y}, Dante, τ_m, 90°_{y}, $acq_{\pm}$

The selective excitation DANTE sequence is used to invert the magnetization of an enriched ^{13}C site in one of the components. The peak intensities measured after suitable mix times (τ_m) are determined by any spin diffusion occurring and T_1. T_1 can be measured independently using a similar sequence without the DANTE pulses (2). The measurements have been made on a Bruker WM250 equipped with an IBM solids accessory and a Doty probe. Our 90° pulses are 5.5μs and the DANTE necessary to complete inversion contains 18 pulses of .8μ sec separated by 75μs. This allows for a suitable excitation width for CP/MAS polymer lines and the DANTE sidebands are spaced sufficiently out of the normal spectral width. The original equipment has to be

be changed to allow for the large number of pulses in the sequence and for the use of long mix times. Accurate setting of the ^{13}C pulse power is crucial and the data is best acquired using block averaging.

The CP/MAS spectra shown below are for a solid blend of Bisphenol-A Polycarbonate (BPAPC) with 25% di-nbutylphthalate (DBP). Selective inversion of one ^{13}C enriched carboxylate on the DNP is accomplished using the above sequence. Spin diffusion can be observed between the carboxyl of DNP and the protonated aromatic (1,2) and the quaternary aliphatic (3) peak of BPAPC. The methyl peak (4) decay is dominated by a short T_1.

Sincerely,

Paul Inglefield

Paul T. Inglefield,
Ajoy K. Roy,
Alan A. Jones

(1) P. Caravatti, G. Bodenhausen and R.R. Ernst, J. Mag. Res. 55 88 (1983).
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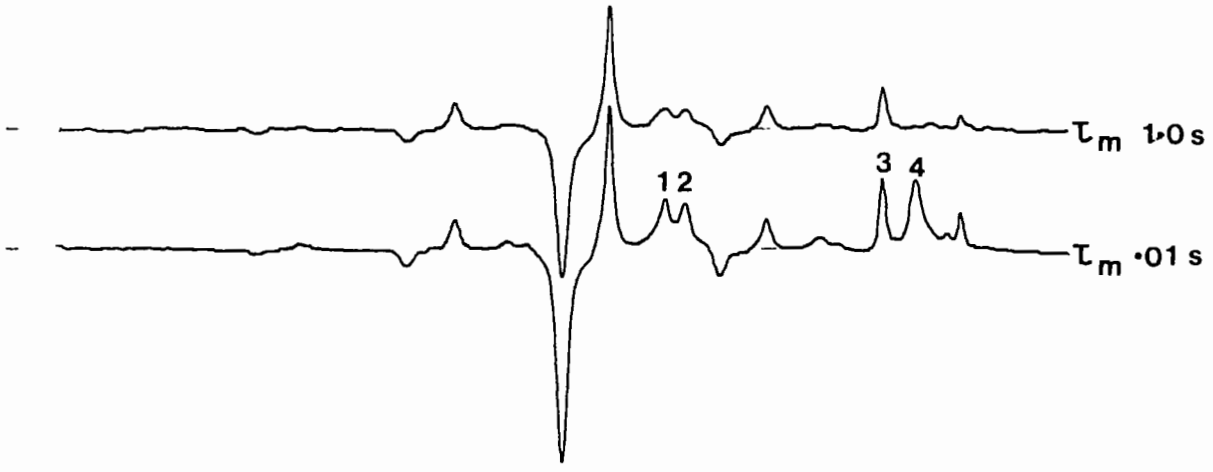


STATE UNIVERSITY LEIDEN - THE NETHERLANDS
GORLAEUS LABORATORIES - DEPARTMENT OF CHEMISTRY

P.O. Box 9502, 2300 RA Leiden Phone: 71-148333, extension: 3919

Your letter:
Your ref.:
Our reference: CE/RC

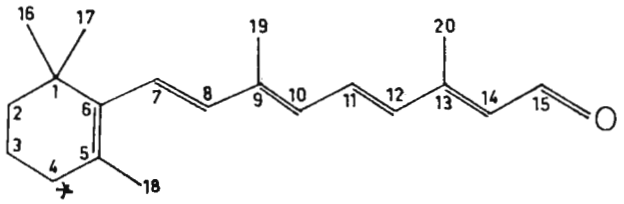
LEIDEN, April 7th, 1986

Subject: ^{1}H NMR with ^{13}C decoupling

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

Dear Professor Shapiro,

Everybody nowadays routinely runs ^{13}C NMR spectra with ^{1}H decoupling. For us however, the otherway around (^{1}H [^{13}C]) also is interesting. For our investigation on vision and bacteriorhodopsin photochemistry we use selective ^{13}C enriched (92%) retinals. To check the ^{13}C incorporation and to measure the ^{13}C-^{1}H coupling constants it is sometimes necessary to have a ^{13}C decoupled ^{1}H spectrum, especially for the compounds with ^{13}C labeling on more than one carbon.
For this purpose we use the 5mm BB probe from the WM-300. This probe has a very good proton resolution (ODCB $\leq$ 0,1Hz) on the decoupling channel. The BB channel, tuned for ^{13}C, is used as decoupling channel for the BSV-3-BX heterodecoupling unit.
As an example you see in fig. 2 the ^{1}H NMR spectrum of 4-^{13}C-all-trans retinal.
The lower trace shows the undecoupled spectrum (high field part); in the upper trace the spectrum is ^{13}C decoupled. (The H4 resonance overlaps with the $9CH_3$).



all-trans-retinal

fig. 1

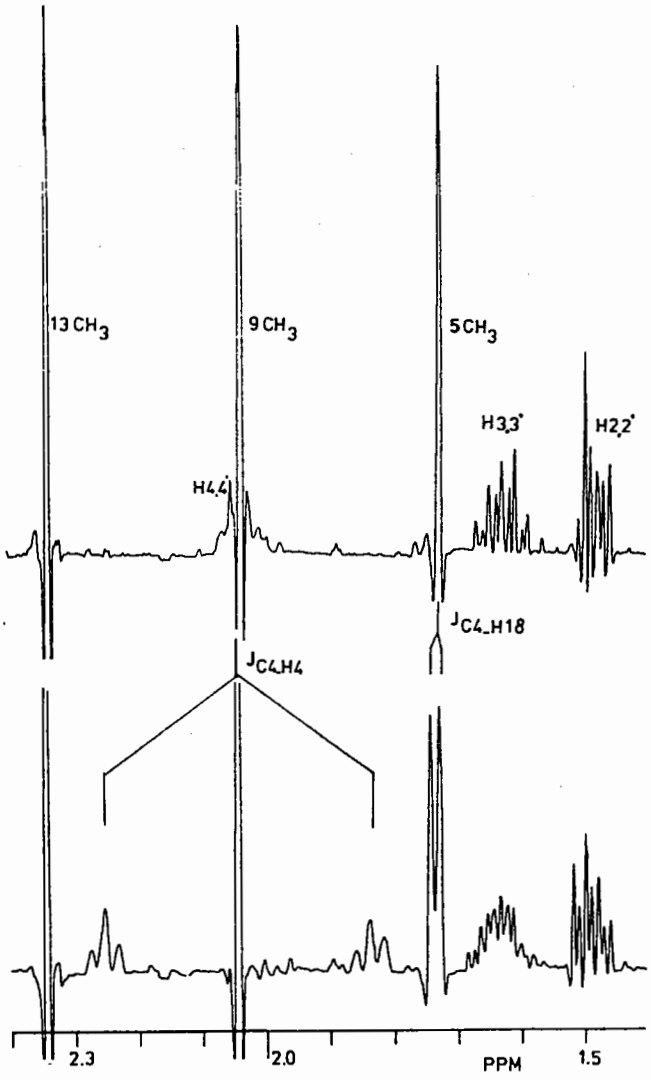


fig. 2

Sincerely yours,

C. Erkelens J. Courtin J.van Haveren J. Lugtenburg

332-62

Weyerhaeuser Company

Tacoma, Washington 98477
(206) 924-2345

April 8, 1986

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

Dear Professor Shapiro:

Subject: PF Resin Cure in the Presence of Wood

I have written a couple of times concerning NMR investigations of phenolic resin chemistry but, to my knowledge, no one has reported NMR studies of the end product: namely, a cured composite of adhesive and wood mimicking the glueline region of plywood. This letter summarizes such a study, on which I collaborated with Dr. R. Scott Stephens, and which will appear in the literature later.

Wood contains numerous functional groups which are reactive to hydroxide at high temperatures, and it is reasonable to expect hydrolysis of hemicellulose acetyls and depolymerization of lignin and cellulose to consume a good bit of the caustic added to phenolic resins to promote their cure. The loss of alkalinity would at least partially neutralize the resin and could affect its cure rate and final structure. Figure 1 illustrates pH effects in the CP/MAS spectrum of a cured resin; the phenoxide C1 peak at 160 ppm in the cured as-is (highly alkaline) resin disappears when the resin is neutralized to pH 9 as these species are protonated to phenols. Also, the neutralized resin contains more methylene ether linkages (65-75 ppm) and methyl groups (25 ppm), both of which are mechanically weaker than methylene linkages (30-40 ppm).

Not surprisingly, these effects are seen when the alkaline resin is cured with wood. Figure 2A is the spectrum of such a composite. Subtracting out the appropriate wood spectrum, we have the bottom trace in Figure 2, showing the resin spectrum in the composite. The phenol C1 resonance indicates nearly complete neutralization of the resin alkali, warning us that the cured adhesive probably is not as strong as it could be.

The significance is not so much that my S-100 is a good solid-sample pH meter, but rather that different species of wood, which exhibit a wide range of buffer capacity toward hydroxide, should differ widely in their interference with resin cure.

Respectfully,

Larry

Larry W. Amos

LWA:ckw2C/0404/e31

Enclosures

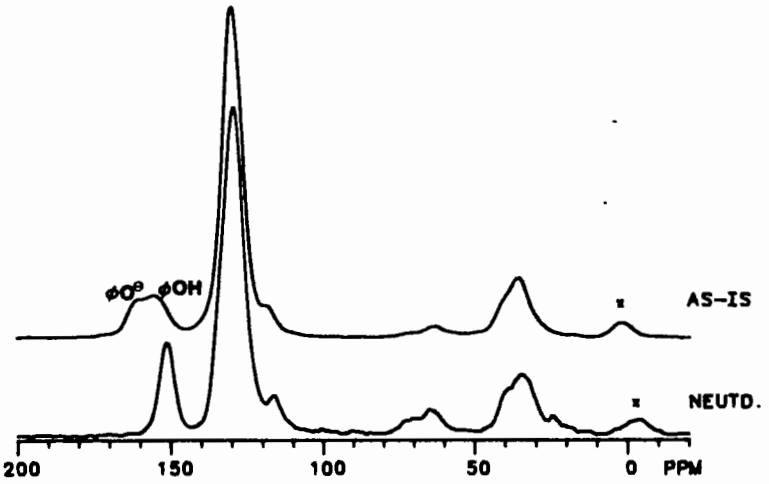


Fig. 1. Effects of Resin pH on the CP/MAS NMR Spectrum of a PF Adhesive Cured at 200°C for 15 min.

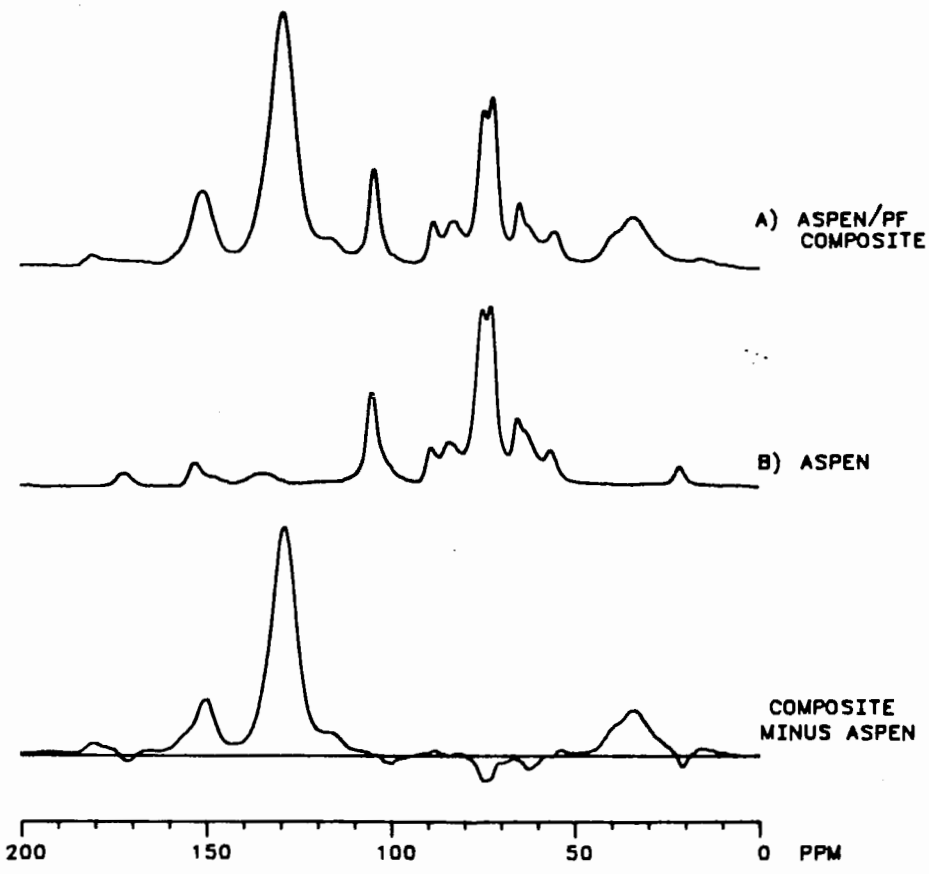


Fig. 2. Subtraction of Two Spectra, Yielding the Spectrum of the Cured Adhesive in a Composite.

INSTITUT FÜR PHYSIK DER UNIVERSITÄT BASEL
EXPERIMENTELLE KERNPHYSIK
Klingelbergstrasse 82, Telefon 061 - 44 22 80
Prof. Dr. P. Diehl

CH - 4056 Basel (Schweiz) April 9, 1986

Prof. B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843
USA

Anharmonic vibrational corrections to dipolar couplings

Dear Barry

In the NMR spectroscopy of partially oriented molecules the direct dipolar coupling constants are normally corrected for effects due to harmonic vibrational motions [1]. The resulting molecular geometry is the so-called r_α structure, which specifies the average nuclear positions. These positions deviate from the equilibrium nuclear positions because of the anharmonic vibrations. The r_α structure can be converted to the equilibrium (r_e) structure, if the anharmonic force field of the molecule is known. This conversion is beginning to be feasible, because the increasing power of ab-initio methods allows the calculation of reliable cubic anharmonic force fields for small molecules. For this reason, we have looked into the significance of the anharmonic vibrational contributions to the dipolar couplings of hydrogen cyanide, using the force field of Nakagawa and Morino [2].

The results are shown in the table. As is well known, spurious anharmonicities are introduced by making rectilinear expansions of the vibrational potential energy function, i.e. purely quadratic potential terms in curvilinear internal coordinates contribute cubic and higher terms in a normal coordinate representation of the potential function.

(continued on page 67)

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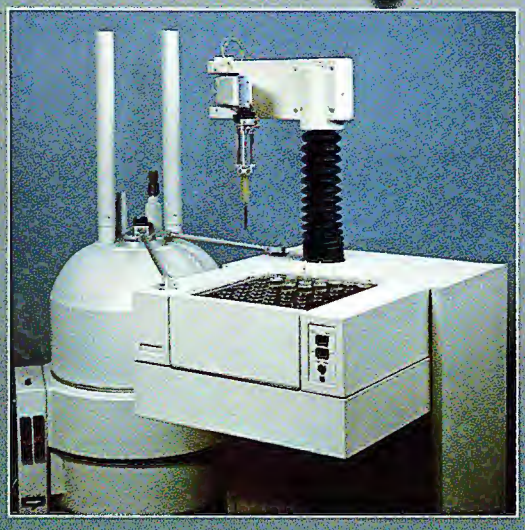

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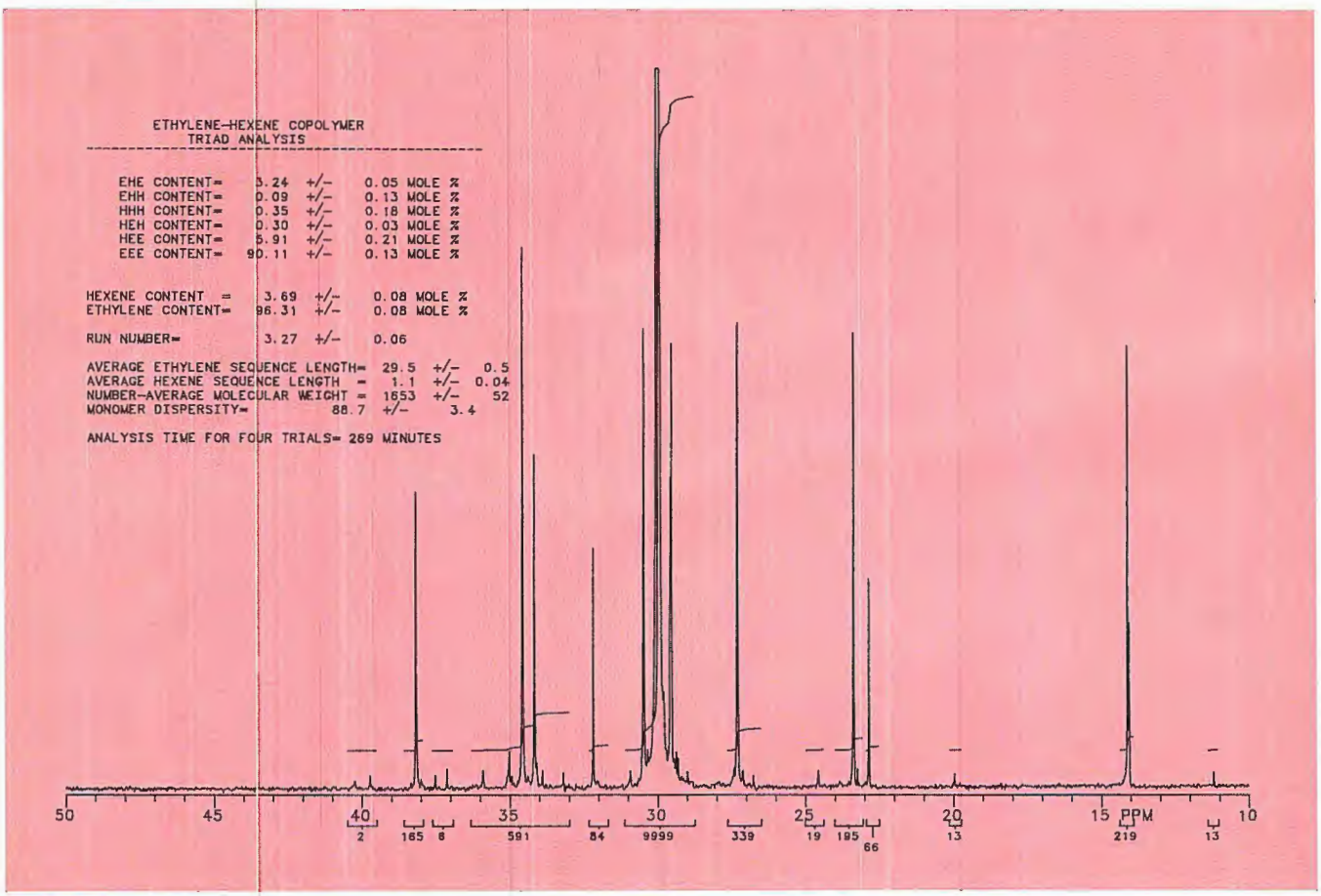

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(continued from page 64)

Table

Vibrational contributions to the dipolar couplings of HCN relative to the equilibrium couplings D^e_{ij} (in per cent): D^h_{ij} = harmonic contributions, D^{aq}_{ij} = cubic anharmonic contribution arising from the quadratic potential terms in internal coordinates, and D^{ac}_{ij} = the corresponding anharmonic contribution arising from the cubic potential terms.

ij	D^h_{ij}/D^e_{ij}	D^{aq}_{ij}/D^e_{ij}	D^{ac}_{ij}/D^e_{ij}	$(D^h_{ij}+D^{aq}_{ij}+D^{ac}_{ij})/D^e_{ij}$
CH	-9.99	5.48	-4.22	-8.73
CN	0.13	0.15	-1.33	-1.05
HN	-1.21	2.71	-2.72	-1.22

This "transformation part" of the anharmonicity is quite important, having the same order of magnitude as the "true" anharmonicity. In our example, as in many other cases, the effects of these two anharmonicities tend to cancel out: when the nuclei move around arcs of circles in the bending vibrations, the average internuclear distances (calculated from the average nuclear positions) tend to decrease, whereas the Morse-like anharmonicities of the stretching vibrations tend to increase the average internuclear distances.

With best regards

Sincerely yours

J. Lounila P. Diehl

References

[1] S. Sýkora, J. Vogt, H. Bösiger, and P. Diehl, J. Magn. Reson. 36, 53 (1979)

[2] T. Nakagawa and Y. Morino, Bull. Chem. Soc. Japan 42, 2212 (1969).

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DEPARTMENT OF BIOLOGICAL CHEMISTRY

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AREA CODE 301

April 17, 1986

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

Dear Barry:

ALL IS NOT ROSY WITH ROESY

Our studies of the conformations of substrates bound to enzymes usually include the determination of interproton distances from time-dependent NOEs. The magnitudes of the NOE observed at resonance A upon pre-irradiation of resonance B for varying lengths of time, together with the selectively-measured longitudinal relaxation time of resonance A, are used to evaluate σ_{AB} the cross-relaxation rate between A and B. σ_{AB} may then be used in the following simple 2-spin equation to determine the distance between A and B (r_{AB}):

$$r_{AB} = (62.02)\left[\frac{1}{\sigma_{AB}}\left(\frac{6\tau_r}{1 + 4\omega_I{}^2\tau_r{}^2} - \tau_r\right)\right]^{1/6}$$

The correlation time (τ_r) is either back-calculated by inserting σ and r values for a pair of protons whose distance apart is known and invariant, or τ_r is measured directly by determining σ at two different frequencies (1).

We have recently investigated the usefulness of obtaining such NOEs in the rotating frame - the CAMELSPIN (2) or 1-dimensional-ROESY experiment (3). Our sample consists of a 1:7 mixture of rabbit muscle adenylate kinase (M_r = 21,700) and its substrate AMP. In this system, conventional NOEs are negative at 250 MHz (Figure 1A); the correlation time is 1.2×10^{-9} s. Rotating-frame NOEs, on the other hand, were positive (Figure 1B). This is as expected from the previous equation, since ω has been greatly reduced in the rotating frame (we estimate $\omega_{rot.} \approx 5.7$ kHz).

The time-dependent development of the rotating-frame NOE was monitored by varying the length of the spin-locking pulse from 0 to 500 ms. The size of the observed NOE for a given spin-lock time (t) depends upon r_{AB}, σ_{AB} and the extent of relaxation of resonances A and B along the y' axis ($T1\rho$). The NOE increases with time to a maximum (t_{max}), and then decreases at longer values of t. In practice, the $T1\rho$ values for the AMP protons were ~200 ms and t_{max} for intramolecular NOEs on AMP ranged from 100-200 ms. Therefore, resonance A was typically substantially reduced in height at the time of maximal NOE so that while (cross relaxed-control) difference spectra yielded Δ peak height values of up to 85% of the partially reduced peak, the actual measureable

NOE_{max} was <9% of the original peak height. This provides no advantage over the conventional NOE experiment for this system, in which NOEs of up to -10% are observed. The situation was also poor for intermolecular rotating-frame NOEs where, due to the rapid relaxation of enzyme protons (~30 ms), only a small time window was available for observing these effects.

One possible use of the CAMELSPIN experiment for enzyme-bound substrates may be the direct evaluation of τ_r from the frequency dependence of σ since the rotating frame provides a second frequency (≈0 MHz) without the need for a second instrument. Evaluation of this potential application is in progress. We would also like to point out that the rotating frame permits easy selective observation of enzyme resonances with comparitively long T1ρ values (compare the aromatic region of the enzyme spectrum in Figs. 1A and B).

(1) Fry, D.C., Kuby, S.A., and Mildvan, A.S. Biochemistry 24, 4680 (1985).
(2) Bothner-By, A.A., Stephens, R.L., and Lee, J. J. Am. Chem. Soc. 106, 811 (1984).
(3) Bax, A. and Davis, D.G. J. Mag. Res. 63, 207 (1985).

Sincerely,

Dave & Al

Dave Fry and Al Mildvan

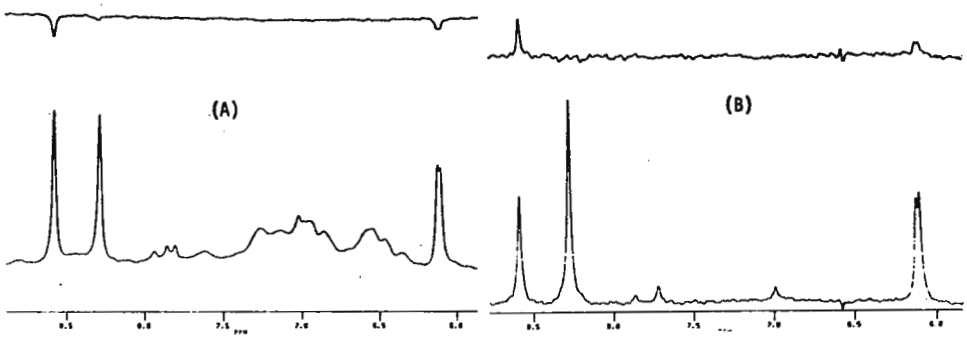

Figure 1. NOEs acquired in the conventional manner (A) and in the rotating frame (B). The sample was 7.8 mM AMP, 1.1 mM adenylate kinase, 1 mM Tris Cl^-, 0.1 mM DTT, and 35 mM KCl in D_2O at pH 7.2. Spectra were acquired on a Bruker WM-250 at 24°C.
(A): Control spectrum acquired using 90° pulse (5.3 μsec) and a recycle time of 5.8 sec. The carrier was placed at 4.7 ppm. Upper spectrum is the difference between a control and a cross-relaxed spectrum in which a 1.0 s preirradiation pulse was applied with the decoupler off-resonance (9.7 ppm) and on the AMP H2' resonance (4.8 ppm) respectively.
(B): Control spectrum acquired using the pulse sequence: RD - 90°x - SLy' (t) - observe, where RD is a 3.2 s relaxation delay and SLy'(t) is a spin-lock pulse along y' maintained for a time (t) of 200 ms. Pulses were administered with the low-power transmitter (90° pulse = 44 μsec). The carrier was placed at 9.4 ppm to avoid Hartman-Hahn effects. Upper spectrum is the difference between a control and a cross-relaxed spectrum in which selective 180° pulse was applied with the decoupler off-resonance (9.7 ppm) and on the H2' resonance (4.8 ppm) respectively.

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CP/MAS NMR on a Narrow Bore Bruker WM-400

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

Dear Dr. Shapiro:

Thank you for the reminder that our next contribution to the TAMU NMR newsletter is now due.

Last summer we took delivery of a Bruker CP/MAS NMR accessory for our Bruker WM-400 NMR spectrometer. This accessory is a retrofit and consists of 2 CP/MAS NMR probes (optimized for ^{15}N and ^{13}C), 3 high power amplifiers for decoupling and cross-polarization, and a pneumatic unit for sample spinning and sample insertion/ejection.

As you are probably aware, cross-polarization experiments on high field narrow bore instruments are often difficult to perform and require a lot of time to set up properly. Although we've had problems with arcing (which have been solved) this accessory has performed as well as one could expect and the time involved in switching from high resolution liquids to CP/MAS is suprisingly short (0.5 - 1 hour).

Shown in Figures 1 and 2 are examples of the resolution and sensitivity typically obtainable for adamantane and sucrose with this accessory.

Yours very truly,

Gord Kennedy
G.J. Kennedy
Chemist

Cathy Michael
Cathy A. Michael
Technologist

/jmb
0491n

c.c. R. Vander Linden

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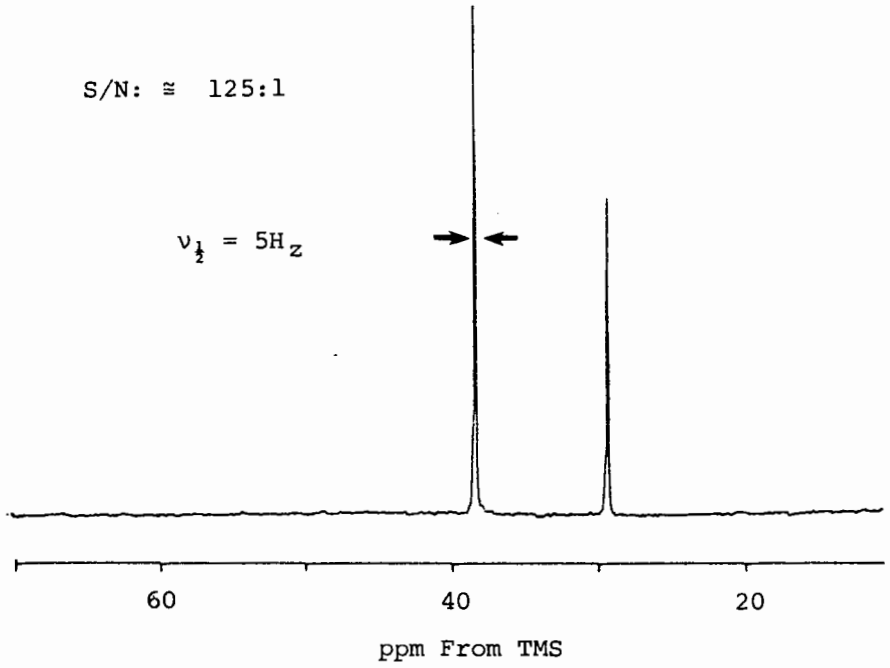

FIGURE 1: 100.6 MHz ^{13}C CP/MAS NMR Spectrum of Adamantane. (NS=1, LB=0, Contact Time = 10 ms)

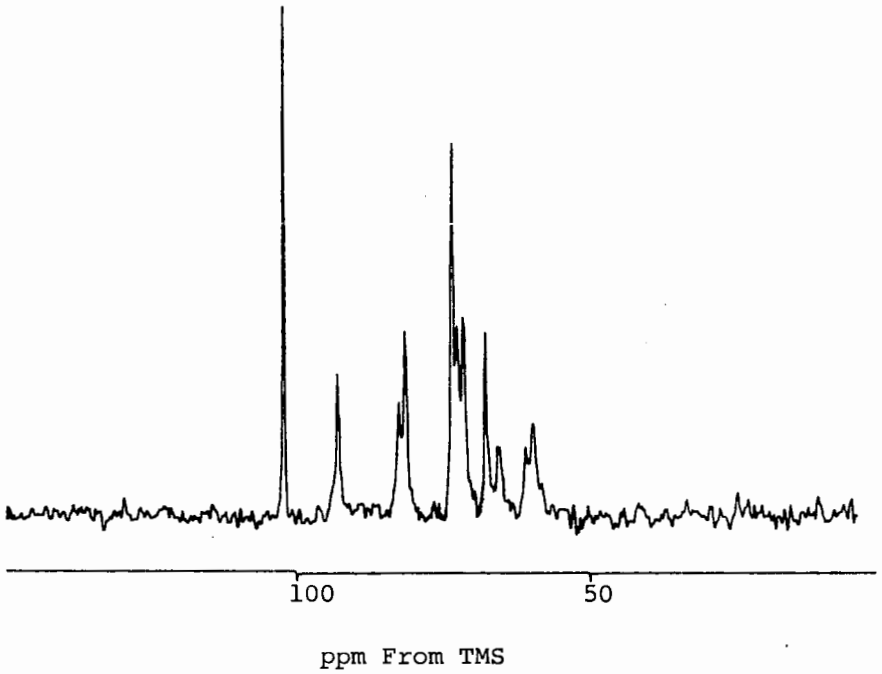

FIGURE 2: 100.6 MHz ^{13}C CP/MAS NMR Spectrum of Sucrose. (NS=100, LB=10, Contact Time = 1 ms)

332-72

Prof. Dr. F.H. Köhler
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Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77 843
USA

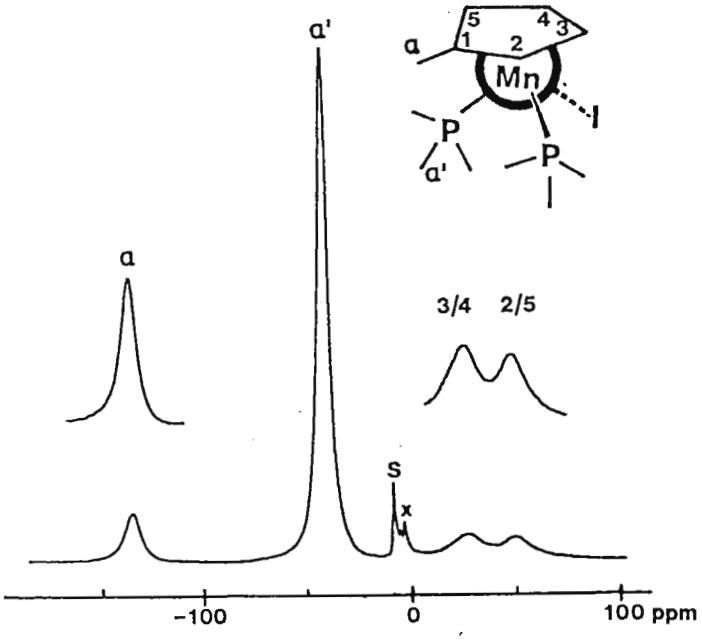
Title: "Isoelectronic" Manganese(II) Complexes as Seen by ^1H NMR

Dear Professor Shapiro,

unexpectedly we continued a story part of which I have told in these letters 323 (1985) 44. The reason is a frequent phenomenon: the molecules under study reacted in a way we had not anticipated. You might remember that we had extracted various informations from the ^1H spectra of paramagnetic manganocenes $(Rcp)_2Mn$, where Rcp means a substituted cyclopentadienyl with R = H, Me,... A main feature was that a $^2E_{2g} \longrightarrow {}^6A_{1g}$ spin crossover can be observed on heating.

We now found, that one Rcp ligand can be replaced by two phosphines and one halide leading to a new class of halfsandwiches. We were pleased to see that the ^1H NMR spectra of these species (one example is given in the figure; S = C_6H_6, x = impurity; temperature: 305 K) is rather similar to those of the original manganocenes. This could be expected if $(Rcp)_2Mn$ and $(Rcp)MnX(PR_3)_2$ are (in a broad sense) isoelectronic.

However, there are some small but important differences. In (Mecp)MnI(PMe_3)$_2$ all Mecp signals are shifted to lower frequency as compared to (Mecp)$_2$Mn at a given temperature. Furthermore, at ambient temperature, the signals of (Mecp)MnI(PMe_3)$_2$ are much narrower than those of the manganocene. While the broad lines for the sandwich reflect fast exchange of $^2E_{2g}$-low-spin and $^6A_{1g}$-high-spin isomers, the halfsandwich is a pure high-spin molecule at 30 °C. The above mentioned signal shifts show that the electron spin delocalization is somewhat different for both manganese(II) complexes. Besides π-delocalization a direct σ-mechanism is operative, and the latter is more important in the halfsandwiches.



In conclusion manganese sandwiches and halfsandwiches are not as isoelectronic as one might think. Even subtle differences are revealed by simple ^1H NMR spectra.

Please credit this letter to the subscription of Prof. H.P. Fritz, as usual.

Yours sincerely,

Frank H. Köhler

Koninklijke/Shell-Laboratorium, Amsterdam

Shell Research B.V.

Professor B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station
TEXAS 77843
U.S.A.

Uw ref.:

Onze ref.: IS 0593

Amsterdam, 26th March 1986
Badhuisweg 3
Tel. via telefoniste (020) 30 91 11
Tel. rechtstreeks (020)
Hr/Mw

Re: Molybdophosphate complexes

Dear Professor Shapiro,

Since our last contribution we have taken delivery of a number of new machines and accessories. In particular, we have acquired an AM-500, which will be used for both liquids and solids; we have exchanged our WM-400 console for an AM-400 console and have added an automatic sample exchanger to this; and finally, we have modified our CXP-200 spectrometer to enable us to do mini-imaging. Not surprisingly, we are therefore hard at work trying out the many new possibilities these changes have opened up and will no doubt report on our efforts in later TAMU newsletters.

Although almost all of our recent TAMU contributions have been concerned with solid-state NMR we have not forgotten that liquid-state NMR still has its uses!

A recent subject of interest to ourselves has been the identification of molybdophosphate species with the aid of phosphorus NMR. Although many techniques have been applied to this problem in the past, ^{31}P NMR was not one of them. As can be seen from the spectra (Fig. 1), these solutions are more complex than has previously been thought.

Koninklijke/Shell-Laboratorium, Amsterdam

Of particular interest was the controversy surrounding the $PMo_9O_{31}(OH)_3^{6-}$ and $PMo_{11}O_{37}^{7-}$ species (known as 9-MPA and 11-MPA respectively) arising from Raman spectroscopy and potentiometric titration measurements ^{31}P NMR however clarifies the situation.These species give rise to the pair of lines around -1 ppm, the exact positions of which are pH-dependent. As can be seen in fig. 2 the peaks actually cross at pH values of about 2.5. It is clear from our work that the resonance labelled (1) in fig. 2 is 11-MPA and the one labelled (2) is 9-MPA.

The full paper has been accepted for publication and should be appearing shortly.
("On the identification of molybdophosphate complexes in aqueous solution", J. Chem. Soc., Dalton Trans., J.A.R. van Veen, O. Sudmeijer, C.A. Emeis and H. de Wit).

Yours sincerely,

KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM

G.R. Hays

O. Sudmeijer

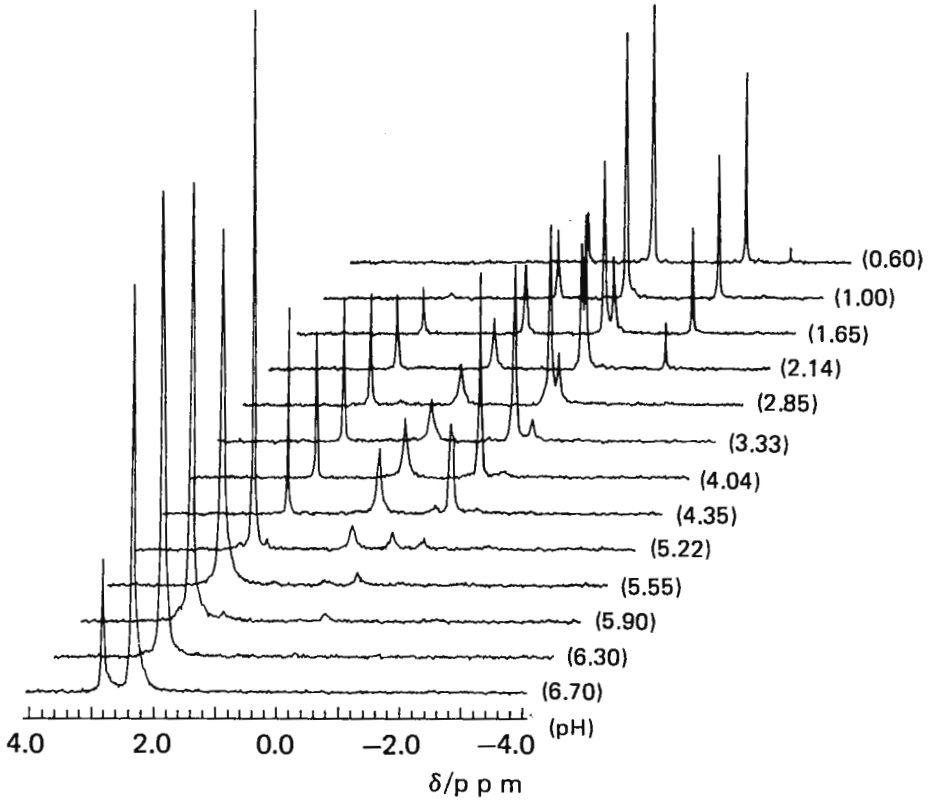


FIG. 1: ^{31}P NMR SPECTRA OF Na_2MoO_4/Na_3PO_4 SOLUTIONS
$[P] = 0.06$ mol/l, $[Mo] = 0.54$ mol/l

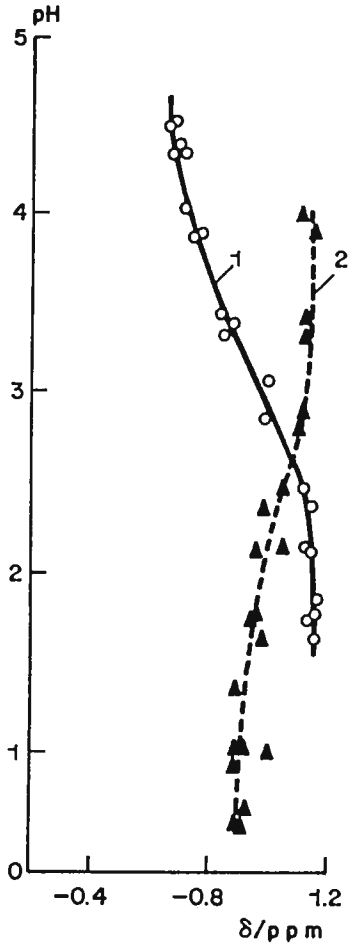


FIG. 2: pH DEPENDENCE OF THE CHEMICAL SHIFT OF THE TWO RESONANCES OCCURRING AROUND $\delta \simeq -1$ ppm THE SIGNALS (1) ARE DUE TO 11 –MPA, AND THE SIGNALS (2) TO 9 –MPA (SEE TEXT)

A Plea For Brevity.

As this issue of the Newsletter dramatically demonstrates, the increased interest in this informal medium of communication, along with our significantly increased mailing list, have conspired to make the brevity of individual contributions an ever more important issue. Contributors to the Newsletter are, therefore, urged very strongly to try everything reasonable in order to keep the Newsletter size from becoming too big to mail. Specific suggestions include:

1. Avoid wide margins: One inch (2.54 cm) is more than adequate, and this should not be exceeded at the sides, top, or bottom.
2. Use of smaller type than the most usual "12-pitch" (i.e., 12 characters to the inch); 13- or 14-pitch is very reasonable, and even 15-pitch will do. (This "editorial" is in 13-pitch.) Nothing smaller than 15-pitch, or larger than 12-pitch, please.
3. Commensurate with the need to accommodate subscripts, superscripts, etc., as well as mathematical symbols, please do not double-space anything which can be either single-spaced or 1.5-spaced.
4. A major space saving can be effected by careful sizing and formatting of figures. Please examine each of your figures (and tables) with a view to presenting them in the smallest format which conveys the information adequately.

In the past it has been suggested that requiring fewer contributions per year per subscriber would help solve Newsletter size problems. Since the current number of contributions is, effectively, one per year, I am not inclined to lessen this minimal frequency of involvement. Only in very exceptional circumstances may an individual contribution exceed three pages.

Finally, my usual plea to provide titles for your contributions.

B.L. Shapiro
25 April 1986

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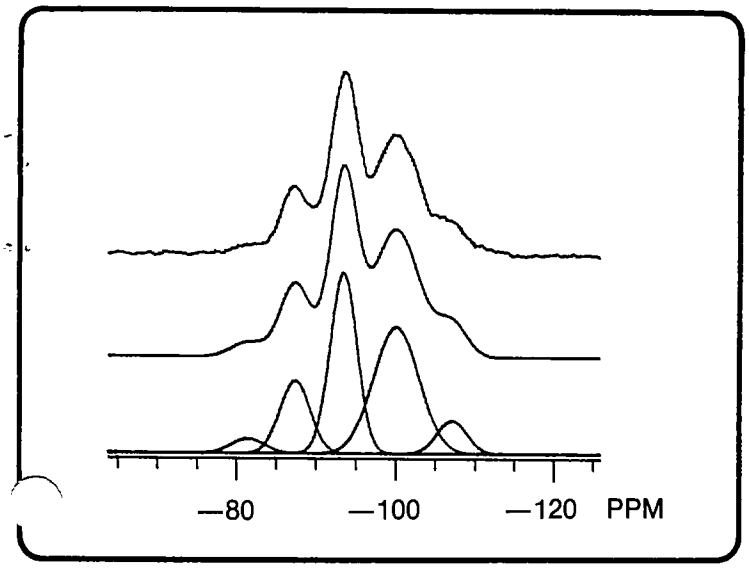
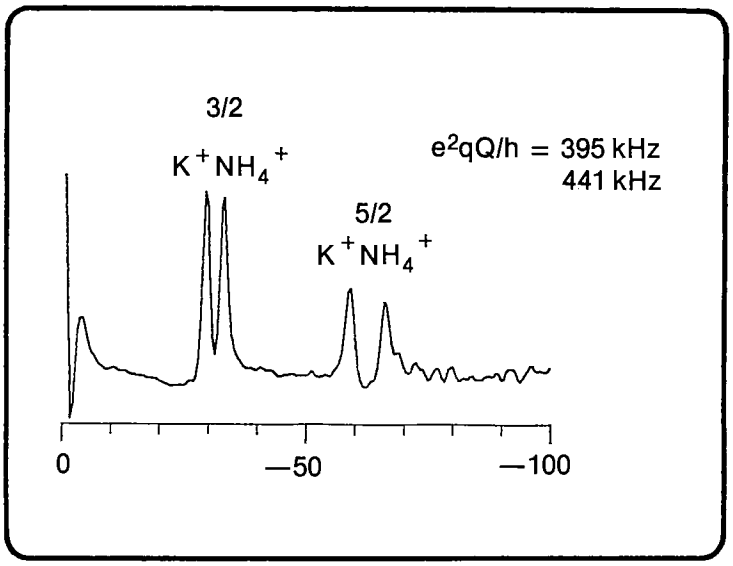


Si-29 MASS + SIMULATION Linde Y



Al-27 QUADRUPOLE ECHO + DEPAKEING
K^+, NH_4^+ - ALUMS

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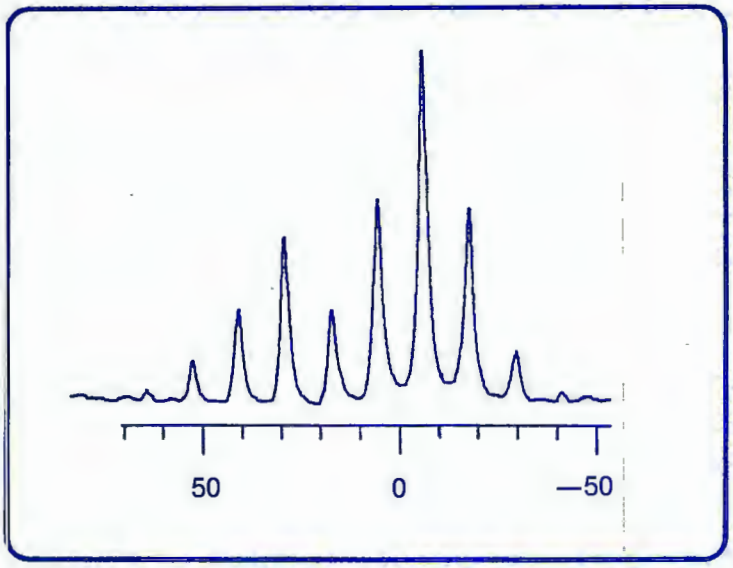
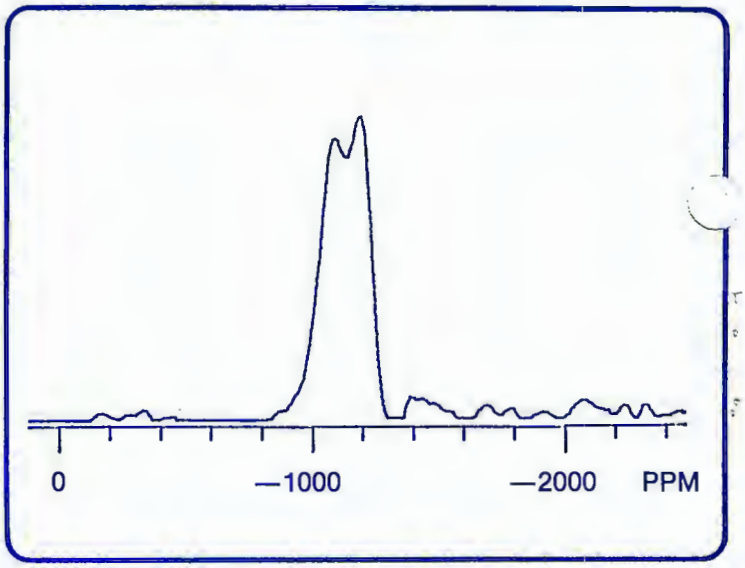


P-31 {H-1} MASS, $(NH_4)_2HPO_4$



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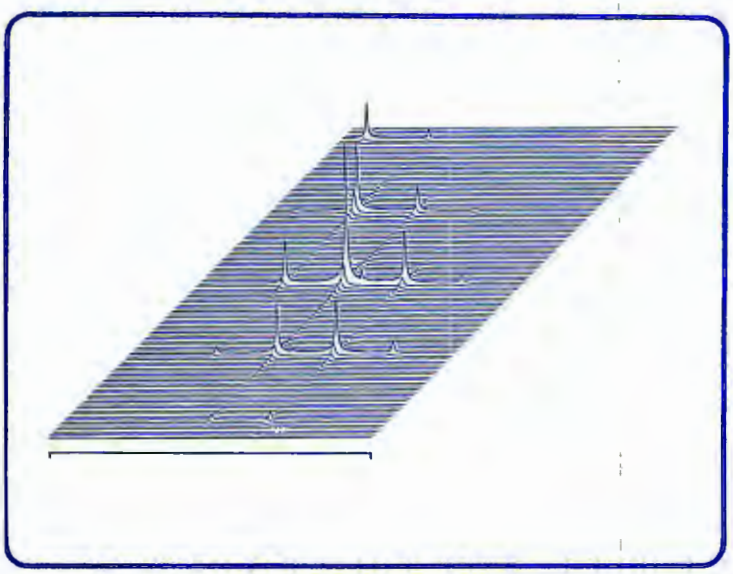
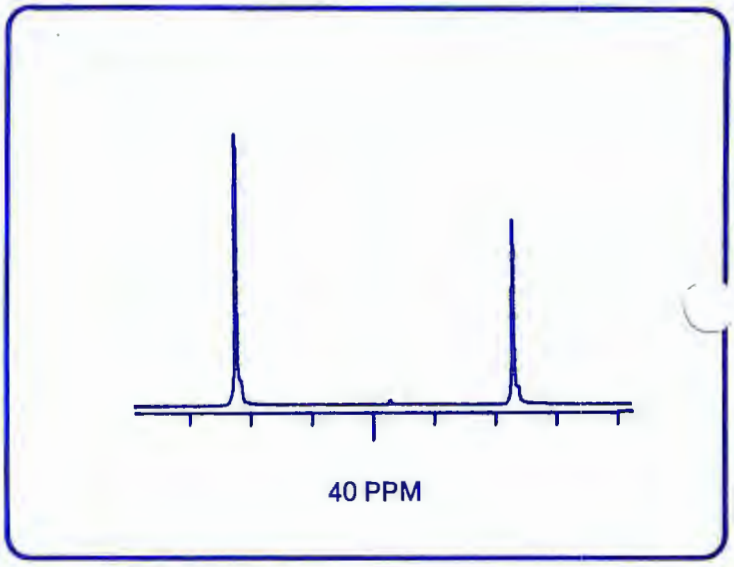
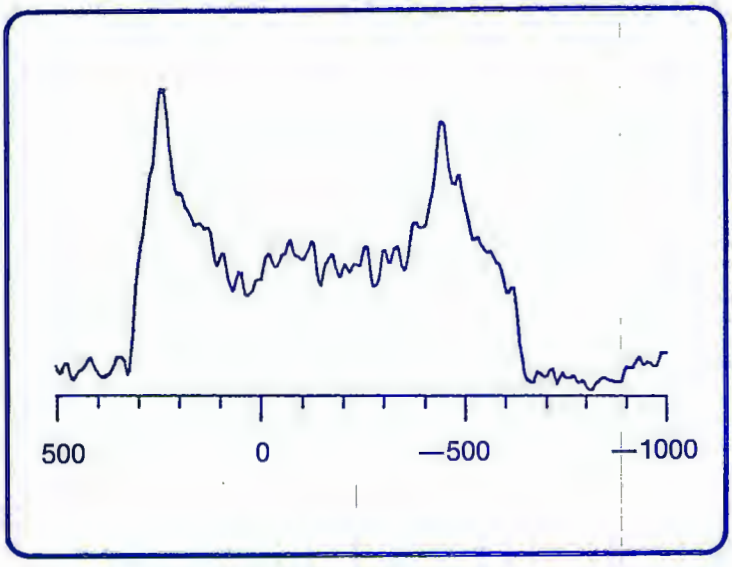


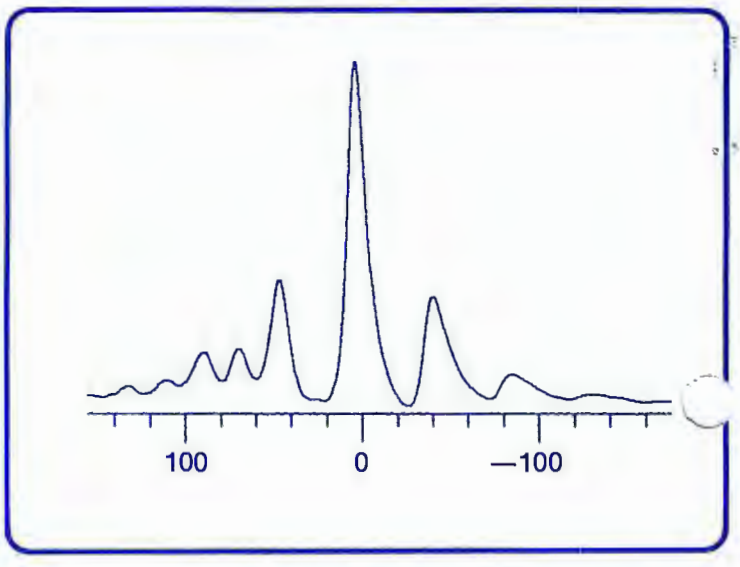
2D NMR OF LIQUIDS



C-13 CP-MASS, ADAMANTANE



K-39 SPIN ECHO, KNO_3



Al-27 MASS, SMECTITE

EASTERN ANALYTICAL SYMPOSIUM, INC.

SILVER JUBILEE EAS - NMR Program 1986
New York Hilton Hotel
New York City, New York

from: Gwendolyn N. Chmurny
Program Committee
301-695-1226

"Fundamental Principles and Applications of Two-Dimensional NMR"

Monday, October 20, 1986 all day EAS short course
R. Andrew Byrd (Chairman), James A. Ferretti, Ad Bax

Starting from a basic understanding of 1D NMR and an awareness of 2D NMR, the fundamentals of the primary conventional 2D NMR experiments will be discussed. These will include homonuclear and heteronuclear shift correlation experiments and cross-relaxation/exchange experiments. The extension of these concepts to the new generation of 2D experiments involving indirect detection, multiple quantum coherence, and net coherence transfer will be covered in greater detail. The principles will be illustrated with actual experimental examples.

All day poster session - 32 posters already accepted

Monday, October 20, 1986
Chairman: C. Anderson Evans

"Twenty Five Years of NMR Spectroscopy - Past, Present and Future"

Tuesday, October 21, 1986 (9:00 am - Noon)
Chairman: Frank A.L. Anet, Department of Chemistry, UCLA, Los Angeles, CA

(1) "Past, Present and Future of High Field NMR Spectroscopy". Frank A. L. Anet, Department of Chemistry, UCLA, 405 Hilgard Ave., Los Angeles, CA 90024
(2) "Past, Present and Future of Theoretical Calculations". Cynthia J. Jameson, Department of Chemistry, University of Illinois - Chicago Circle, Chicago, IL 60680.
(3) "Past, Present and Future of NMR Software". George C. Levy, Department of Chemistry, Syracuse University, Syracuse, NY 13210.
(4) "Past Present and Future of Quadrupolar Nuclei in the Solid State". Eric Oldfield, School of Chemical Science, University of Illinois, Urbana, IL 61801.

"New Frontiers in Applications of NMR Spectroscopy"

Tuesday, October 21, 1986 (2:00 -5:00 pm)
Chairman: Roy H. Bible, Searle R&D, Div. of G. D. Searle Co., 4901 Searle Pkwy., Skokie, IL 60077

(1) "Applications of Two-Dimensional NMR to Structural Elucidations of Complex Organic Molecules". William F. Reynolds, University of Toronto, Department of Chemistry, Toronto, Canada M52 1A1
(2) "Applications of NMR in Pharmaceutical Analysis". George Slomp, Upjohn Co., Physical and Analytical Chemistry, Kalamazoo, MI 49001
(3) "Applications of NMR to Ecological Recognition". David Lynn, University of Chicago, Chicago, IL
(4) "Structure Determination of Desertomycin by Means of Two-Dimensional NMR Techniques". Ad Bax, Laboratory of Chemical Physics, Arthritis Institute, NIH, Bldg. 2, Bethesda, MD 20205

Coffee Break sponsored by Varian Associates, Inc. (5:00 - 5:30 pm)

"Teaching the New NMR: A Multimedia Presentation of Density Matrix Treatment"

Tuesday, October 21, 1986 (5:30 - 6:30 pm)
Chairman: George Mateescu, Chemistry Department, Case Western Reserve University, Cleveland, OH 44106

"Advances in High Resolution NMR Spectroscopy"

Wednesday, October 22, 1986 (9:00 am - Noon)
Chairman: Gwendolyn N. Chmurny, NCI-Frederick Cancer Research Facility, P.O. Box B, Bldg. 467, Rm. 102, Frederick, MD 21701

(1) "Performance Envelopes in the Design of NMR Experiments". Robert E. Santini, Department of Chemistry, #92, Purdue University, West Lafayette, IN 47907
(2) "Two Dimensional NMR Studies of Polysaccharides". R. Andrew Byrd, Dept. of Biochemistry and Biophysics, FDA, Bldg. 29, Rom. 430, NIH, Bethesda, MD 20205
(3) "Structural and Conformational Studies of Biologically Active Peptides in H_2O". James A. Ferretti, Donald G. Davis, and Kathleen S. Gallagher, National Heart, Lung, and Blood Institute, NIH, Bldg. 10, Rm. 7N316, Bethesda, MD 20205
(4) "New Pulse Techniques in Two Dimensional NMR". Ole W. Sörensen, and Richard R. Ernst, ETH-Zentrum Physical Chemistry Lab., CH-8092, Zurich, Switzerland

"NY SAS Award Symposium honoring Professor Paul Lauterbur"

Wednesday, October 22, 1986 (2:00 - 5:00 pm)
Chairman: V. S. Venturella, Anaquest Div., BOC, Murray Hill, NJ 07974

(1) "Opening Remarks: NMR Imaging". Vincent S. Venturella, Anaquest Div., BOC, Murray Hill, NJ 07974
(2) "Applications of Magnetic Relaxation and Spectroscopy". Robert G. Bryant, University of Rochester, School of Medicine, 601 Elmwood Ave., Rochester, NY 14642
(3) "NMR Imaging in Solids". Allen N. Garroway, Chem. Branch, Code 6120, Chemical Div. Naval Research Lab., Washington, DC 20375
(4) "Ultrahigh Resolution NMR Microscopy". Truman R. Brown, Fox-Chase Cancer Center, Philadelphia, PA 19111
(5) "Award Address: The Complete Resonator: NMR Pictures and Spectra of Molecules and Men". Paul C. Lauterbur, University of Illinois, Dept. of Medical Information Science and Chemistry, 1307 West Park, Urbana, IL 61801

"Solid State NMR Spectroscopy"

Thursday, October 23, 1986 (9:00 am - Noon)
Chairman: P. Mark Henrichs, Eastman Kodak Co., Bldg. 81, Research Lab., Rochester, NY 14650

(1) "Multinulear NMR Studies of Protein Dynamics in Solids". Dennis A. Torchia, Yukio Hiyama, and S. W. Sparks, National Institute of Dental Health, NIH, Bldg. 30, Rm. 106, Bethesda, MD 20205
(2) "^{13}C Solid-State NMR of Small Molecules Adsorbed on Supportive Metal Catalysts". Kurt W. Zilm, G. Webb, and D. Simonsen, Department of Chemistry, Yale University, 225 Prospect St., New Haven, CT 06511
(3) "Structural Characterization of Solid Synthetic Polymers With NMR Spectroscopy". P. Mark Henrichs and J. Michael Hewitt, Eastman Kodak Co., Research Labs., Rochester, NY 14640
(4) "Mixing in Magnetic Resonance". C. S. Yannoni, IBM Almaden Research Center, K34-802, 650 Harry Rd., San Jose, CA 95120-6099

"NMR Spectroscopy and Imaging in Biological Systems"

Thursday, October 23, 1986 (2:00 - 5:00 pm)
Chairman: Robert S. Balaban, Laboratory of Kidney and Electrolyte Metabolism, National Heart, Lung and Blood Institute, NIH, Bldg. 10, Bethesda, MD 20205.

(1) To be announced. Robert S. Balaban, Laboratory of Kidney and Electrolyte Metabolism, National Heart, Lung and Blood Institute, NIH, Bldg. 10, Bethesda, MD 20205.
(2) To be announced. Robert G. Shulman, Dept. of Molecular Biophysics and Biochemistry, Yale University, New Haven, CT 06511.
(3) To be announced. Britton Chance, Director, Johnson Research Foundation, University of Pennsylvania, D501 Richards G-4, Philadelphia, PA 19104.
(4) To be announced. Joseph J. Ackerman, Department of Chemistry, Washington University, St. Louis, MO 63130.

"Contributed Papers"

Friday, October 24, 1986

"NMR Workshop"

Tuesday, October 21, 1986 PM

Exhibitors as of 3-5-85:

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12

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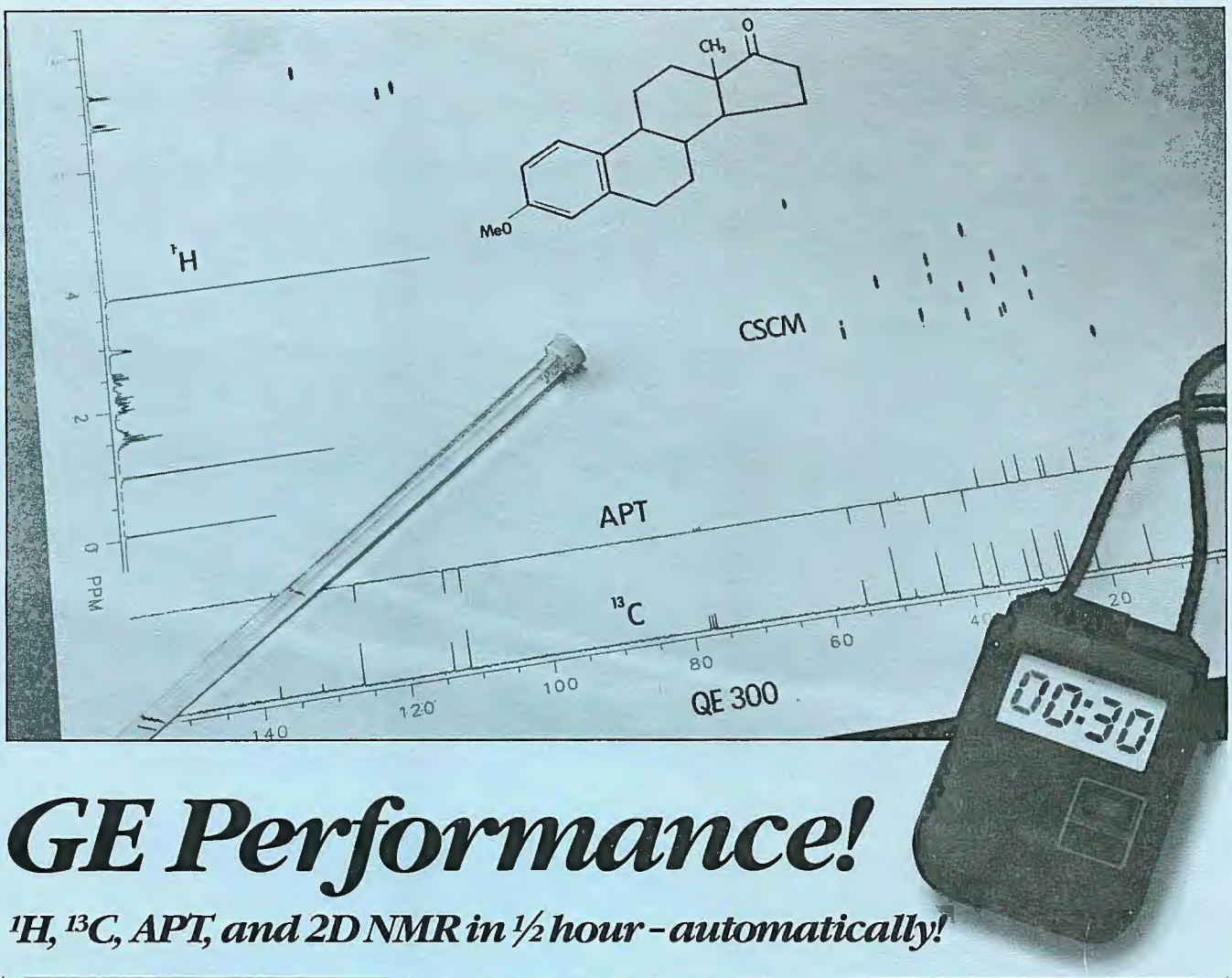

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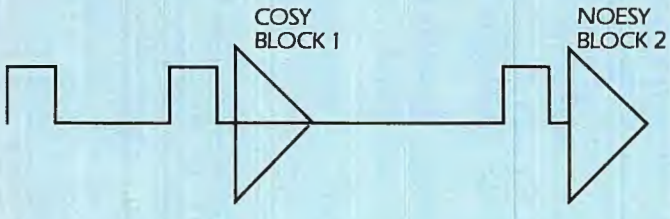

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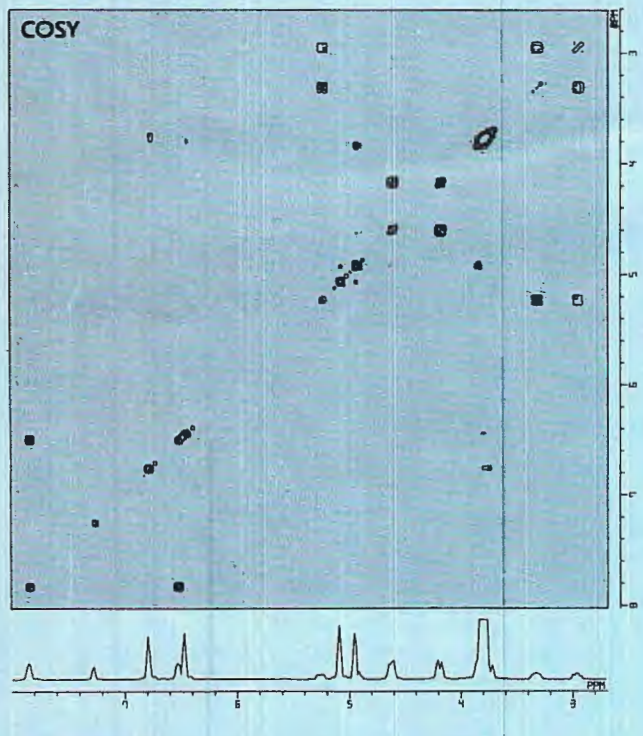

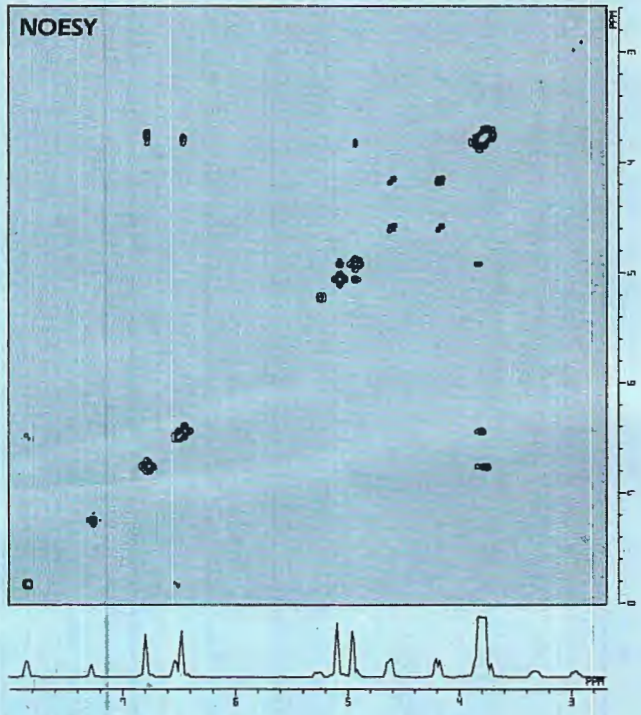

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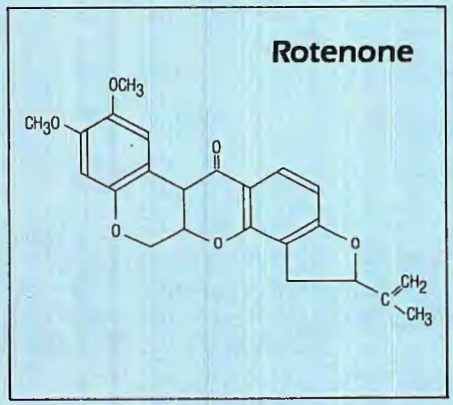

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