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**FORTHCOMING NMR MEETINGS** (Additional listings are solicited)

**8th Rocky Mountain Regional Meeting** - June 8-12, 1986; Denver Convention Complex; Denver, Colorado; Meeting Chairman: William E. Beard, USDA-ARS, P.O. Box E, Ft. Collins, Colorado 80522.

**4th International Symposium on NMR Spectroscopy** - June 16-20, 1986; Tabor, Czechoslovakia; Chairman: Dr. Petr Trska, NMR Laboratory, Institute of Chemical Technology, Suchbatarova 5, CS-166 28 Prague 6, Czechoslovakia.

**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, Università 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, Università 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 Newsletter No. 329, p. 23 and Newsletter No. 325, p. 27.

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.

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 Department of Chemistry  
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U S A

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OUR REF:

YOUR REF:

pH effects on  $^1\Delta N(D)$  of the ammonium ion

Dear Professor Shapiro,

The large difference between deuterium isotope effects on  $^{14}\text{N}$  nuclear shielding,  $^1\Delta N(D)$ , in ammonia and the ammonium ion has recently attracted much interest <sup>1-3</sup>.  $^1\Delta N(D)$  of the ammonium ion are similar in the three papers, but not identical (see Table 1).

The study of less symmetrical amines and ammonium ions showed similar effects.  $^1\Delta N(D)$  of aniline showed clearcut solvent effects, whereas amides showed no such effects <sup>3</sup>. We, Antonin Lycka and I, suggested that the lone-pair in amines is a determining factor and that hydrogenbonding likewise is important. It looks also as though pH plays a role. We have looked further into this problem and have preliminary arrived at the following for the ammonium ion:

$^1\Delta N(D)$		pH	Ionic strenght
1.05	4 M $\text{NH}_4\text{NO}_3$ in 3 M $\text{HNO}_3$	$\sim - 0.5$	3.5 M
1.17 <sup>1</sup>	4 M $\text{NH}_4\text{NO}_3$ in 2 M $\text{HCl}$	$\sim - 0.3$	3.0 M
1.32	1 M $\text{NH}_4\text{Cl}$ in 1 M $\text{HCl}$	$\sim 0$	1 M
1.15 <sup>2</sup>		2 $\sim$ 3	
1.03	1 M $\text{NH}_4\text{Cl}$ in $\text{H}_2\text{O}$	4.75	1 M

From these data it looks like differences in pH can explain the variations in the values given in the litterature <sup>1-3</sup>.

The negative isotope effect on  $^1\text{H}$ ,  $^1\Delta\text{H(D)}$  of ammonium ion has also given rise to some discussion<sup>4,5</sup>. We are presently looking into this old problem and I wonder if somebody else have collected isotope effects on similar compounds.

1. R. E. Wasylishen and J. O. Friederich, J. Chem. Phys., **80**, 585 (1984).
2. V. D. Tarasov, V. I. Privalov, U. A. Buslaev and U. Eichhoff, Z. Naturforsch., **39 b**, 1230 (1984).
3. A. Lycka and P. E. Hansen, Magn. Reson. Chem., **23**, 973 (1985).
4. G. Fraenkel, Y. Asahi, H. Batiz-Hernandez and R. A. Bernheim, J. Chem. Phys., **44**, 4647 (1966).
5. M. Shporer and A. Loewenstein, **15**, 9 (1968).

Yours sincerely



Poul Erik Hansen



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Thank you for your help in this matter.

Sincerely,



Bruce S. Lamb, Ph.D.  
Research Scientist



Department

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Date February 27, 1986.

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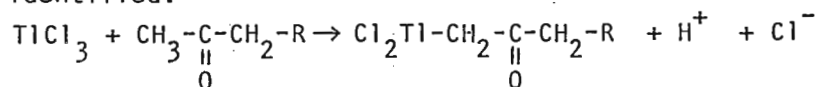
Dear Prof. Shapiro,

Novel Monoorganothallium(III) Compounds Identified by  $^{205}\text{Tl}$  NMR

You do not always get what you want. But sometimes the unwanted may be quite interesting.

In our studies of thallium(III) halide complexes in aqueous solutions we wanted to slow down the chemical exchange between the different  $\text{TlCl}_n^{3-n}$  species by decreasing the temperature so that we would see separate Tl NMR peak for each of the species. In order to avoid freezing we added some acetone.  $^{205}\text{Tl}$  NMR spectrum of the resulting solution still showed only one peak for all the exchanging species. However, after some time we could observe the spectrum showed in Fig. 1, where in addition to the usual peak at about 2700 ppm there is a triplet of quartets at about 2800 ppm.

Replacing the solvent water by  $\text{D}_2\text{O}$  does not change anything, but replacing acetone by acetone- $\text{d}_6$  produces a broad peak instead of the triplet. Hence, we assign the triplet to the Tl-H spin-spin coupling in a Tl-acetone compound. We have also added other aliphatic ketones to  $\text{TlCl}_n^{3-n}$  solutions and from the splitting patterns of the  $^{205}\text{Tl}$  NMR spectra the following reaction could be identified:



(R = H,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ )

if  $\text{TlCl}_3$  is assumed to be the reacting thallium complex.

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The reaction can be manipulated by changing several parameters: Cl/Tl-ratio, ketone/Tl-ratio, temperature, acidity level, concentrations etc. Thus, different Tl-organo compounds can be obtained.

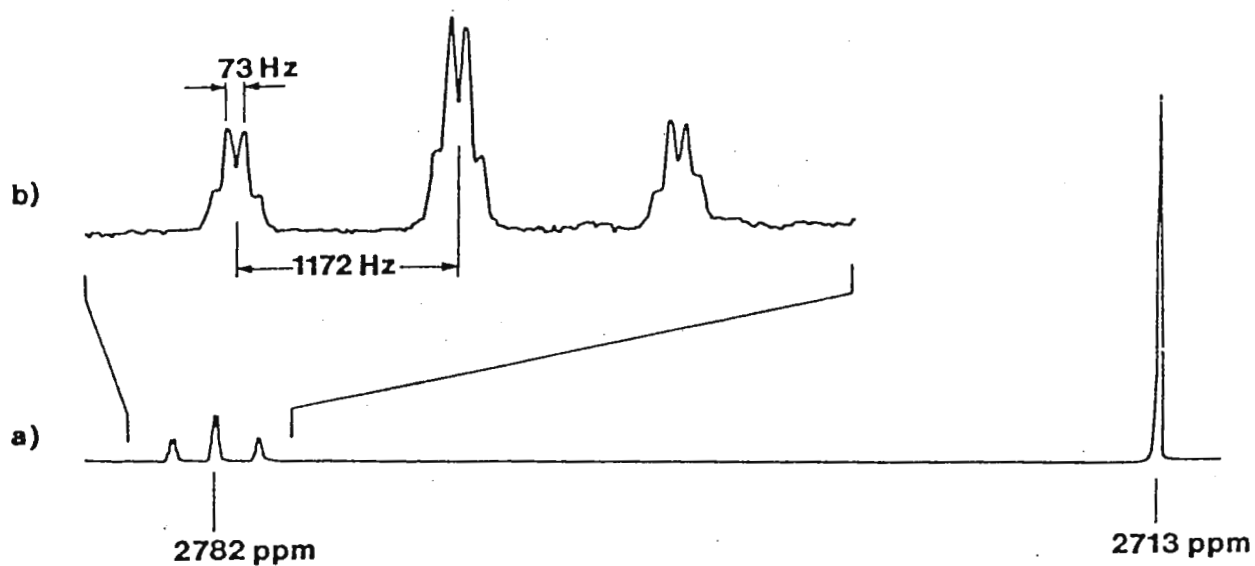


Fig. 1. 51.9 MHz  $^{205}\text{Tl}$ -NMR spectra of an aqueous solution containing Tl(III) and  $\text{Cl}^-$  few hours after addition of acetone.

a) full spectrum, b) thallium-organic region expanded

Sincerely,  
*Julius Glaser*  
 Julius Glaser

Imre Toth



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pH Dependence of Internal References in Micellar Systems

Dear Prof. Shapiro:

during some pH-titration studies of opioid peptides in sodiumdodecylsulfate (SDS) micelles, we observed that the methyl resonance of TSP, likewise in water [1], shows a long range manifestation of the carboxyl titration. However, by using the function proposed by A. De Marco for water solutions [1], we were not able to completely correct for the pH dependence of the TSP chemical shift. Therefore, the same study was repeated by adding dioxane as a second internal reference.

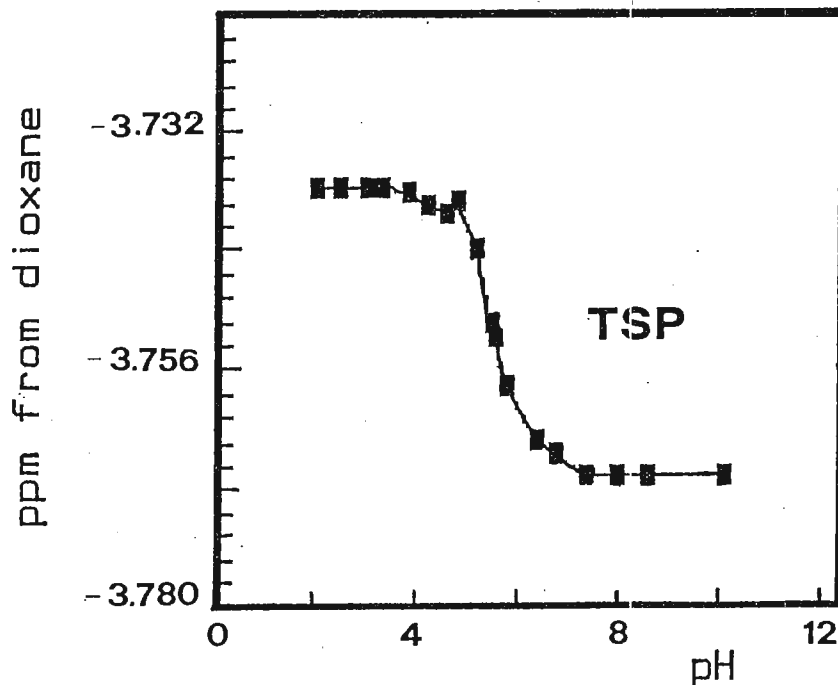
As it appears in Fig.1, the pKa value of TSP in SDS micelles is 5.5 (5.0 in water) and the  $\Delta\delta$  is 0.029 ppm (0.019 ppm in water).

Sincerely yours

(Lucia Zetta)

(Antonio De Marco)

1. De Marco, A. (1977) J. Magn. Reson. 26, 527-528.



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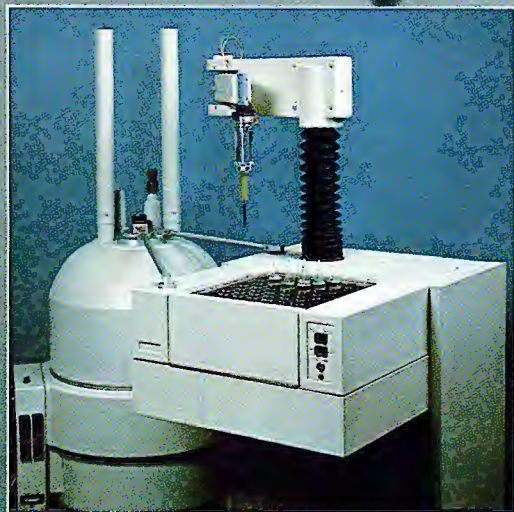


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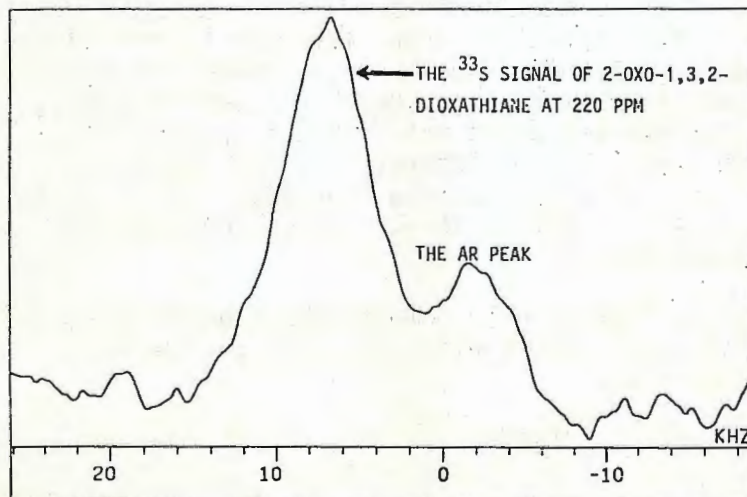
Professor Bernard L. Shapiro  
 Department of Chemistry  
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Dear Professor Shapiro

### $^{33}\text{S}$ NMR Spectra of Some Cyclic Sulphites

We found recently that 2-oxo-1,3,2-dioxathianes give extremely broad signals in  $^{33}\text{S}$  NMR. In such a case acoustic ringing (AR) can become a serious problem when measuring the spectra. First we tried to avoid the AR effect by using  $\pi/2$  -tau - $\pi/2$  pulse sequences with different parametrisation. However, the best results were obtained by a simple single-pulse experiment without any noise decoupling of protons. The instrument dead time and the delay time before acquisition had to be adjusted very carefully to minimize acoustic ringing without losing the whole sulphur signal. This led to a compromise where we still had some acoustic ringing but the  $^{33}\text{S}$  signal was at its strongest (see the example). Neat liquids were used for the measurements.

Thereafter the  $^{33}\text{S}$  spectra of several methyl-substituted 1,3,2-dioxathianes could be measured. However, very little or no conformational information can be obtained from the spectra since the shift effects expected are of the same order of magnitude as the half widths (6 kHz or more) of the signals observed. The complete results will be published shortly.



*Kalevi Pihlaja*  
 Kalevi Pihlaja

*Jorma Mattinen*  
 Jorma Mattinen

György Dombi

MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
CAMBRIDGE, MASSACHUSETTS 02139

JOHN S. WAUGH  
A.A. NOYES PROFESSOR OF CHEMISTRY

ROOM 6-235  
TEL. (617) 253-1901

February 27, 1986

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

Homonuclear Cross-Polarization:  
More Complicated Than You Thought.

Dear Barry:

NMR experiments have gotten so complicated that handwaving is sometimes not enough to understand them, and indeed can be misleading. A case in point is the J-correlation method recently described by Bax and Davis (J. Magn. Res. 65, 335 (1985)). The goal is to obtain broadband spin-propagation through a proton network through the agency of the J-couplings. Normally this doesn't happen because the various protons are detuned from one another by their differing chemical shifts:

$$\mathcal{H} = \sum_i \delta_i I_{zi} + \sum_{i < j} J_{ij} I_i \cdot I_j \quad (1)$$

But suppose a broadband heteronuclear decoupling sequence is applied. Such sequences have the property that they carry all protons through a null rotation irrespective of their shifts, as if all the shifts had been made to vanish. From that point of view Eq. (1) would appear to degenerate into a pure scalar coupling hamiltonian. Indeed the experiment works, but the rate of spin propagation is observed to decrease substantially for protons of appreciably different shifts, even over the range for which heteronuclear decoupling is essentially perfect. Is this because of some instrumental imperfection, or genuine?

Fig. 1 shows the latter to be the case. A pair of spins was subjected (in a computer) to an MLEV16 sequence with  $\gamma B_1/2\pi = 100J$  and the progress of their difference magnetization followed as the chemical shift difference was increased from 0 to 100J. The plot shows the FT of the difference magnetization: if the simple hypothesis were correct there would be ridges at  $\pm J$  and nothing else. Evidently as  $\delta$  is increased two things happen: the effective exchange frequency decreases (but not uniformly) and peaks appear at zero frequency, corresponding to some part of the magnetization which is not transferred at all. The effective hamiltonian (which can be extracted by the computer) depends on  $\delta$  in a complicated way. Other decoupling sequences (WALTZ 16 etc.) behave similarly, though they differ in detail in ways which would not be suspected from their heteronuclear decoupling behavior.

This is but one example of an increasingly common situation in which neither intuition nor pencil and paper theory will work, and one has no recourse except to computer simulation.

Yours,



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 System HH  
 01-14-1986

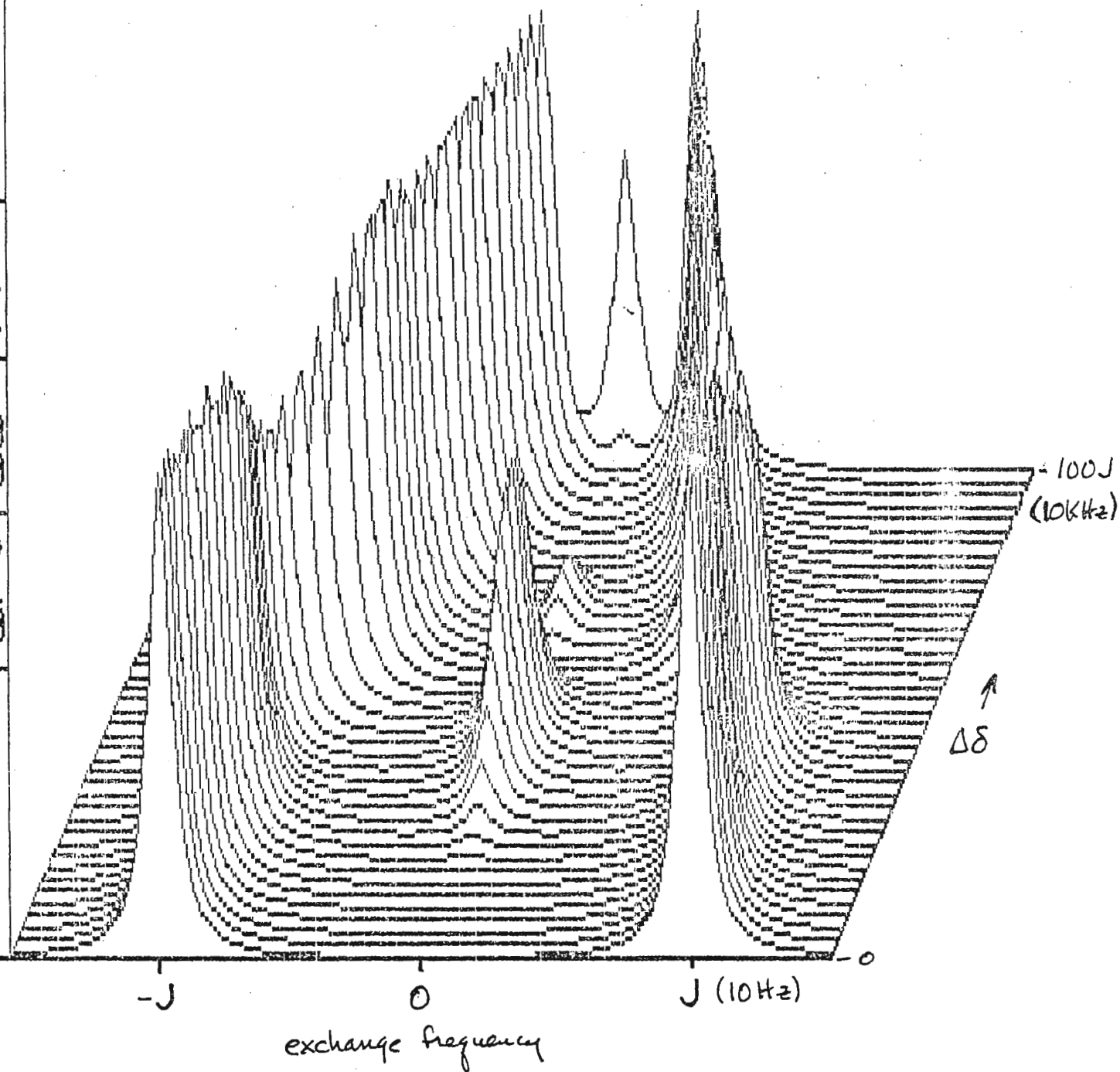
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 to +1.563E+01

Y: HAM (fac)  
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 to +1.000E+00

Z:  $\text{Re}\langle DZ \rangle / \langle DZ0 \rangle$   
 from +5.270E-01  
 to +5.489E+00

Command: h

Row 41/41





## DEPARTMENT OF HEALTH &amp; HUMAN SERVICES

Public Health Service  
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Professor B.L. Shapiro,  
Texas A&M University  
College Station, Texas 77843

National Institute of Arthritis,  
Diabetes, and Digestive and  
Kidney Diseases  
Bethesda, Maryland 20205  
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Room : 109  
(301) 496- 2848

CP performance of MLEV-17

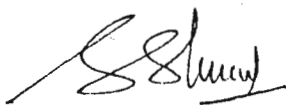
Dear Barry:

In last year's letter, we showed that magnetization transfer via the homonuclear Hartmann-Hahn effect (HOHAHA) (1,2) may have some advantages over more established 2D NMR methods for determining  $^1\text{H}$ - $^1\text{H}$  connectivity information. The most suitable mixing sequence for routine use, we find, is a modified version (3) of the MLEV-16 sequence, used previously for broad-band decoupling purposes (4). This so-called MLEV-17 sequence provides mixing over a fairly wide band-width with very modest rf power. Some of our more recent efforts concentrated on an attempt to measure scalar couplings from the build-up rate of cross peaks in 2D HOHAHA spectra. While quantifying these results, we found that the mixing efficiency and the magnetization transfer rate had a stronger dependence on rf offset than expected. Considering that an rf field strength of p kHz easily decouples a bandwidth of  $\pm p$  kHz, we expected to cover a similar bandwidth for the HOHAHA experiment. Unfortunately, the application to isotropic mixing (1) is much more critical than for broad-band decoupling. Here we demonstrate how the efficiency of the MLEV-17 sequence drops as a function of resonance offset.

As a test, we observe magnetization transfer between the C5H and C6H protons in uridine, an AX system with  $J_{AX}=8.35$  Hz. After an initial  $90^\circ$  pulse, the C5H and C6H magnetization vectors are allowed to become exactly antiphase before switching on the MLEV-17 for a time  $t_1$ . The carrier is positioned on the C5H resonance. The C5H magnetization, present at the end of the mixing period of duration  $t_1$ , ideally should be modulated by the  $J_{AX}$  coupling constant because of oscillatory exchange of the antiphase C5H and C6H magnetization vectors. A Fourier transform with respect to  $t_1$  shows the efficiency of this magnetization transfer. This 2D experiment is then repeated for a series of different rf field strengths. A set of  $F_1$  cross sections taken through these 2D spectra at the C5H  $F_2$  frequency is shown in Figure 1. It is clear from this figure that even for relatively small values of  $\text{offset}/\nu_{rf}$  the mixing is not ideal. Not only does the transfer rate decrease at smaller rf field, but there is also a component of the C5H magnetization that does not get transferred at all, giving rise to the zero frequency contribution.

Initially, we suspected that pulse imperfections caused this undesirable behaviour of the MLEV-17 sequence. However, recent computer simulations by J.S. Waugh suggest that the imperfection of the MLEV-17 sequence probably is of a fundamental nature. His simulations apply to the MLEV-16 sequence, which shows a similar but less dramatic change as a function of  $\text{offset}/\nu_{rf}$ . The advantage of MLEV-17 over MLEV-16, when used for CP, is that MLEV-17 is much less sensitive to pulse imperfections. Under ideal conditions, however, MLEV-17 is probably inferior to MLEV-16. We intend to use an ingenious program, developed by Technic de Bouregas, for verifying these and other ideas.

Sincerely,

  
S. Subramanian

  
Donald G. Davis

  
Ad Bax

1. L. Braunschweiler and R.R. Ernst, J. Magn. Reson. 53, 521 (1983).
2. D.G. Davis and A. Bax, J. Am. Chem. Soc. 107, 2820 and 107,7197 (1985).
3. A. Bax and D.G. Davis, J. Magn. Reson. 65,355 (1985)
4. M.H. Levitt, R. Freeman and T.A. Frenkiel, J. Magn. Reson. 47, 328 (1982).

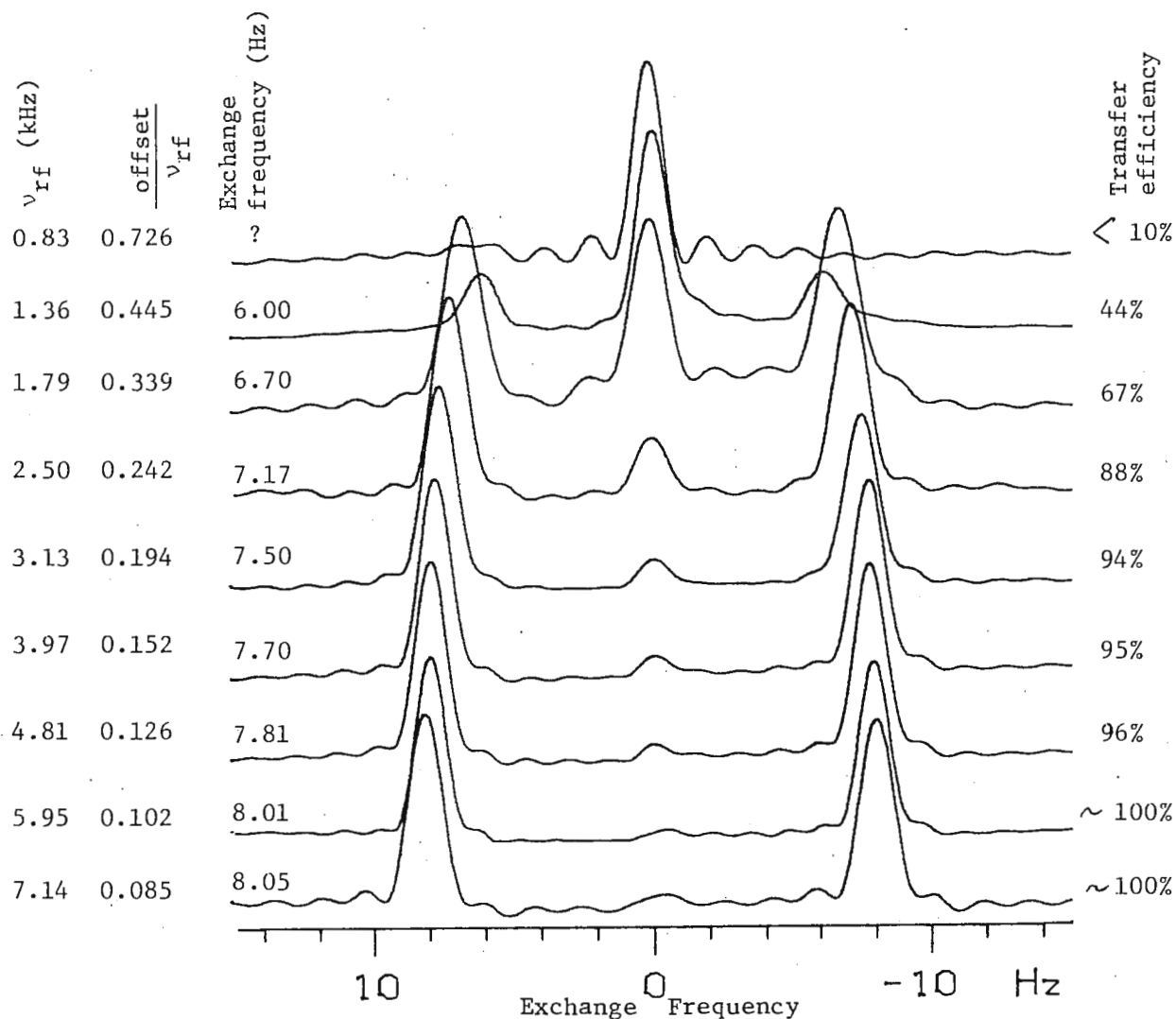


Figure 1. Experimental performance of MLEV-17 for homonuclear Hartmann-Hahn transfer, for different values of  $\nu_{rf}/\text{offset}$ . Each trace represents a cross-section through a 2D experiment in which the cross polarization time ( $t_1$ ) is incremented. For smaller rf fields (top traces) the exchange frequency decreases and a significant component of the magnetization (at zero frequency) is not transferred at all.



The University of Texas  
Health Science Center  
at Dallas

Department of Radiology

Southwestern Medical School  
Southwestern Graduate School  
of Biomedical Sciences  
School of Allied Health Sciences

March 18, 1986

Dr. Bernard Shapiro, Editor  
TAMU NMR Newsletter  
Department of Chemistry  
Texas A&M University  
College Station, TX 77843

In Vivo <sup>31</sup>P NMR Studies

Dear Dr. Shapiro:

This is a report on some recent work which is presently underway in the NMR laboratory at The University of Texas Health Science Center at Dallas. The application of high resolution NMR for the evaluation of metabolic events in vivo has been a central focus of our research efforts for the past two years. Over the past six months, we have focused strongly on the evaluation of phosphate metabolism in the intact heart utilizing two different physiological models to perturb oxygen delivery directly by providing very low levels of inspired O<sub>2</sub> or by an indirect means through the induction of a markedly reduced blood flow as a consequence of loss of total blood volume. The initial focus of these studies was the evaluation of brain metabolism and the results were generally uniformly uninteresting as a consequence of the highly protected status of the brain in mammals. Thus, the very last organ to suffer is the brain.

The next step was to study the kinetics of changes in the bioenergetics of the heart under the same conditions where the total oxygen availability to the intact heart is reduced. The application of <sup>31</sup>P NMR to the intact heart requires that both respiratory and the normal heart cycle motions be minimized. This was done utilizing a simple, but effective, system which provided a dual event gating to both respiration and the normal intrinsic heart cycle utilizing the capabilities of a Coulbourn physiological monitoring system. This unit has the ability to provide simple TTL functions including "ANDING" such that a condition is made that two events must occur simultaneously to provide a data acquisition trigger which is then sensed by the Nicolet 1280 computer used for these studies. The second aspect of the motion issue is that of providing a radio frequency transmit and pick-up coil which does not have wide variations in its tune and match properties as a function of heart motion. This was done using a novel design of a copper wire circle attached to flexible braided copper leads which allows the coil to move freely with the motion of the heart.

The results reported herein were obtained on a 30cm clear bore, 1.9T magnet manufactured by Oxford Instruments. This magnet is interfaced to a Nicolet Magnetics Corporation (now GE/NMR) NT-broadband console and is controlled by a Nicolet 1280 computer. A series of typical spectra are shown in figure 1. Each spectrum is the result of 256 transients acquired at one second intervals for a total time of slightly over four minutes. The series of spectra show the effects of varying the rf pulse width to the 1-turn, 2cm diameter coil which has been placed directly on the left ventricular heart muscle. It is of interest to note that even at the 10 $\mu$ sec pulse interval there appears to be a peak at approximately 6ppm corresponding to 2,3 DPG in the ventricular blood pool. It is also clear from these spectra that under control conditions there is little if any free inorganic phosphate detectable in the normal well-oxygenated heart muscle. One additional point worth noting is that it is possible to routinely obtain spectra in 45 to 60 seconds, having only a small reduction in signal-to-noise compared to the spectra shown in figure 1.

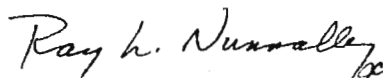
We are pleased to begin our current contribution to the newsletter with this report, and look forward to being active contributors in the future.

Sincerely yours,



George G. McDonald, Ph.D.

and



Ray L. Nunnally, Ph.D.

jlc

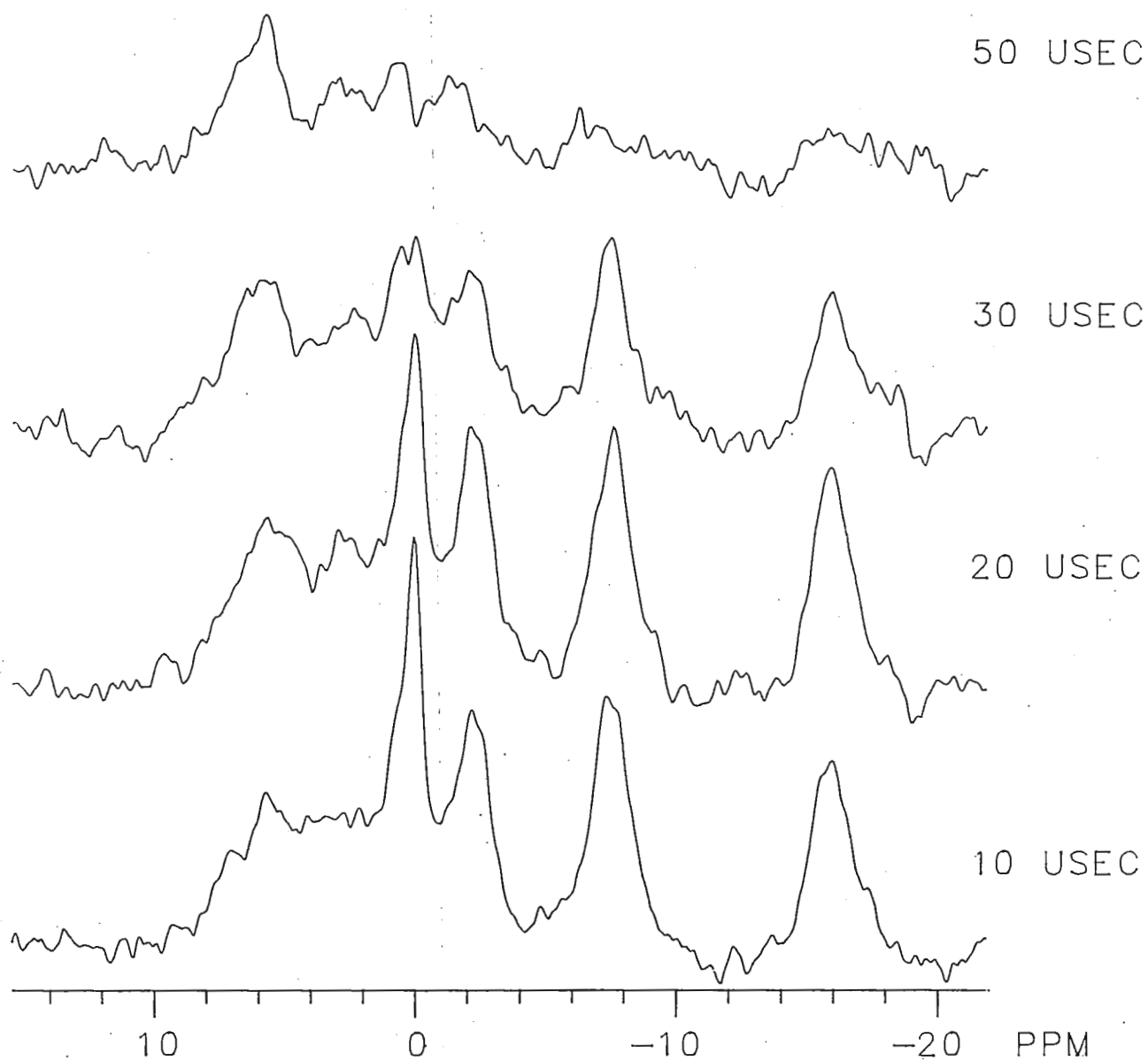


FIGURE 1. Effect of pulse width on  $^{31}\text{P}$  spectrum in heart using a one-turn 2cm diameter coil sutured to the left ventricle. Short pulse widths emphasize the PC and ATP signals from the myocardium while long pulse widths emphasize the 2,3DPG in the ventricular blood.

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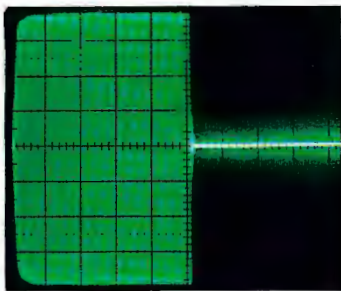
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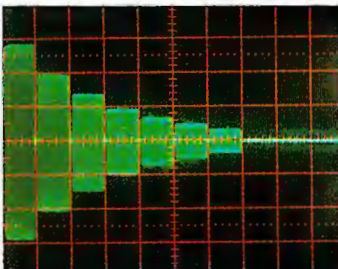
A 5 $\mu$ sec  $^1\text{H}$  observe pulse. ▽



15° phase shift through 360°. ▶



Shaped decoupler pulse. ▶



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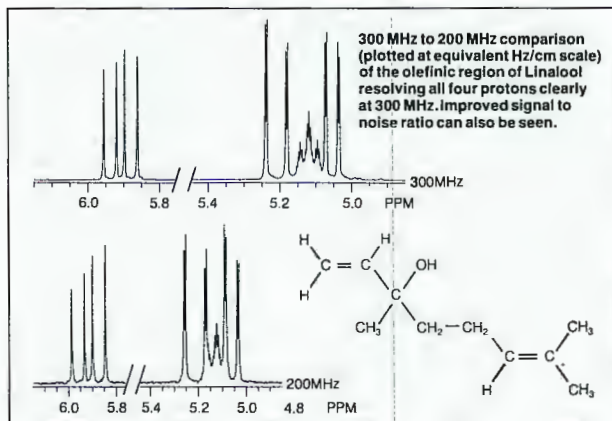
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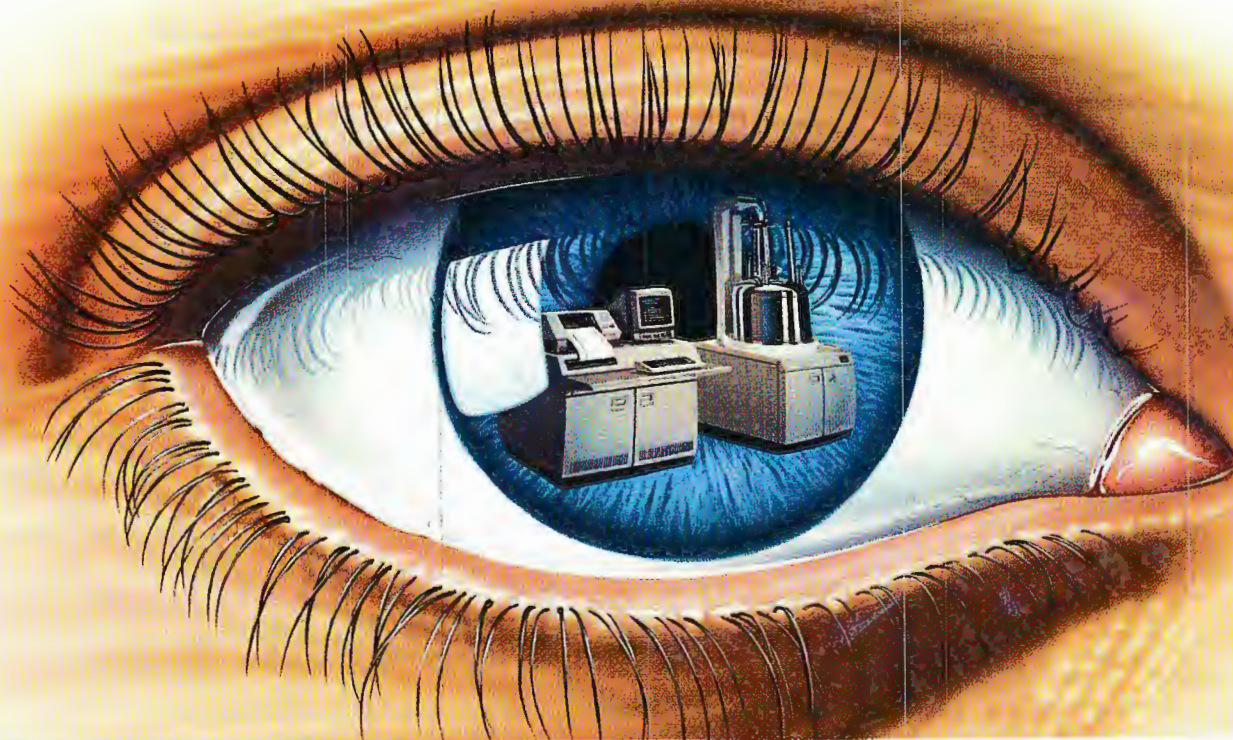
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## See what you've been missing.

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The University of Texas  
Health Science Center  
at Dallas

Department of Radiology

Southwestern Medical School  
Southwestern Graduate School  
of Biomedical Sciences  
School of Allied Health Sciences

March 18, 1986

Establishment of a Regional In Vivo NMR Facility  
at the University of Texas Health Science Center  
at Dallas; Positions Available.

Dr. Bernard Shapiro, Editor  
TAMU NMR Newsletter  
Department of Chemistry  
Texas A&M University  
College Station, TX 77843

Dear Dr. Shapiro:

This letter accompanies our initial report to the Newsletter since taking up resident in Texas some five years ago now. It is with some pleasure that I would like to let the readers of the Newsletter know of the establishment of a Regional In Vivo NMR Facility at The University of Texas Health Science Center at Dallas under the auspices of the NIH Biotechnology Resource Program. This facility will be acquiring a 40cm, 4.7T bore combined spectroscopy and imaging system which will have time available for interested scientific users under the mission of the NIH-sponsored resource facility program. The specific interest and expertise of the NMR group at UTHSCD is in four principal areas. These are: a) the studies of cardiac function and metabolism utilizing high-resolution NMR spectroscopy and proton and fluorine imaging, b) the evaluation of cancer metabolism utilizing high-resolution NMR techniques, c) the development of instrumentation hardware and software, and d) the development of applications of in vivo NMR spectroscopy to the evaluation of metabolic conditions in models relevant to pediatrics (this includes organ transplantation). Thus, we are able to provide strong support in these specific areas to outside users, but do not wish to imply that we would limit the types of studies to be performed at the facility to those areas.

As a consequence of the establishment of this facility and the existence of substantial instrumentation resources and funded projects within the NMR group, we are in the process of recruiting a number of individuals to become participating members of our team. First, let me briefly enumerate the equipment which is currently available for NMR-based research. At the present time there are three vertical-bore, superconducting magnet systems consisting of a 9cm, 7T high-resolution NMR system; a 10cm, 4.7T high-resolution NMR system, and a 13cm, 4.2T magnet-based system which has full capabilities for both imaging and spectroscopy. All of these systems are Nicolet-based computer and console units. In addition, we have a 30cm, 1.9T horizontal Oxford magnet

system interfaced to a Nicolet broadband spectrometer system. This unit is capable of doing spectroscopy only. Last, we are in the process of constructing a 1 meter bore, 1.8T combined spectroscopy and imaging system for clinical research purposes. These five systems are in addition to the 40cm, 4.7T magnet system which is being ordered at the present time. The NMR facilities include extensive rf and digital test gear, complete facilities for rf coil design and testing, and good machine shop facilities for fabricating essential components for NMR system development. There are also two VAX 11/750 computer systems complete with array processors and high resolution image display processors which are resources devoted 100% to NMR research projects.

The NMR group is seeking post-doctoral fellows or research scientists with a strong interest and/or expertise in:

1. NMR instrumentation - with specific interests in computer hardware and software for in vivo NMR spectroscopy and magnetic resonance imaging.
2. The development of methods and applications for time-shared  $^{31}\text{P}$  and  $^1\text{H}$  high-resolution NMR spectroscopy of tumors in vivo (utilizing various types of cancer therapy and the evaluation of the kinetics of metabolic impairment as a consequence of the therapy).
3. To participate in  $^{31}\text{P}/^1\text{H}/^{13}\text{C}$  high resolution NMR studies of cardiac metabolism in situ (perfused) and in vivo utilizing models of myocardial disease and dysfunction.
4. To participate in a project based upon  $^{19}\text{F}$  magnetic resonance imaging using novel  $^{19}\text{F}$ -labeled compounds to assess regional bulk-flow velocities, regional perfusion (tissue transit times), and potential markers of cell damage in both cardiac studies and tumor studies. One area of application is the evaluation of specific perfluorinated compounds for the assessment of tumor oxygenation.

Thank you very much for providing the chance to let the NMR community know about the NMR facility at the Health Science Center and the opportunities which are currently available for pursuing NMR related research.

Sincerely yours,

*Ray L. Nunnally*

Ray L. Nunnally, Ph.D.  
Associate Professor and  
Director, Biomedical Magnetic  
Resonance

TELEPHONE  
345 1844  
  
TELEGRAMS  
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**The University of Melbourne**  
DEPARTMENT OF ORGANIC CHEMISTRY

21st March, 1986 *Parkville, Victoria 3052*

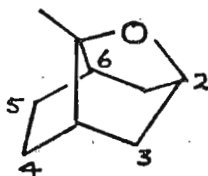
Professor B. L. Shapiro,  
Department of Chemistry,  
Texas A & M University,  
COLLEGE STATION. TEXAS. 77843.  
U.S.A.

Dear Barry,

A Novel Tricyclic Ether

The latest development in this Department is the arrival of a GX-400/54 spectrometer (at long last!) which will complement our other JEOL instruments (FX-100, FX-90Q, PMX-60). Although the installation is not quite complete (e.g., array processor still to come) we have been using it in a routine manner to solve the structures of some compounds generated by our research students.

For example, the tricyclic ether (I) was identified by both 1D and 2D (COSY 45) experiments as the major product of the quench (MeOH/MeONa) of a superacidic solution of 8-methyl-endo-tricyclo-[3.2.1.0<sup>2,4</sup>]octan-syn-8-ol. With the assistance of Mr Bob Schoenfeld, retired Editor of the Australian Journal of Chemistry and now a member of this Department, we have named this novel compound as 6a-methylhexahydro-2,6-methano-2H-cyclopenta[b]furan.



	<sup>1</sup> H	<sup>13</sup> C
2	4.31 (t, 4.9Hz)	74.91 (d, 155Hz)
3,7	1.22 (d, 10.5, <u>endo</u> )	42.65 (t, 131)
	2.15 (m, 10.5, 4.9, <u>exo</u> )	
3a,6	1.89 (m)	44.03 (d, 137)
4,5	1.68 (m, <u>endo</u> )	28.10 (t, 130)
	1.89 (m, <u>exo</u> )	
6a		93.80 (s)
CH <sub>3</sub>	1.45 (s)	17.52 (q, 125)

Our hybrid spectrometer, based on VARIAN, DIGILAB and DEC equipment (TAMU 191-2), which has operated well for about ten years, has been switched off and will be disposed of as soon as possible. Once the internal (University) formalities are complete the equipment will be offered for sale, of which I shall give you due notice.

With best wishes.

Yours sincerely,

*David Kelly*

D. P. Kelly.

DPK:EC

## UNIVERSITY OF CALIFORNIA, DAVIS

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SANTA BARBARA • SANTA CRUZ

UCD NMR FACILITY

DAVIS, CALIFORNIA 95616

March 20, 1986

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

HETHOM

Dear Professor Shapiro:

Recently we were faced with the necessity of performing "sequential" hetero/homo proton decoupling on our Nicolet spectrometers. The basic problem was to produce a hetero-type decoupler saturation pulse (for solvent suppression, as an example), then followed by homonuclear decoupling during acquisition. This could only be achieved on our spectrometers by flipping a homo/hetero switch on the decoupler console panel on each scan, which struck us as rather inconvenient.

To automate the procedure, we have instituted the following. First, the two spectrometers in question are an old NT-360 with 293B pulse programmer and an NM-500 with 293C pulse programmer. Both programmers contain unused timer outputs that can be user-defined. It was necessary to rewire the decoupler control logic board to place the hetero/homo mode switching under software control from the pulse programmer output. The wiring changes necessary are relatively straightforward, and a copy of our wiring modification is available by contacting us. We wrote a pulse sequence called HETHOM, utilizing the new capability.

HETHOM  
HETERO SAT/HOMO DEC  
#1: D7,N0,T,Z  
#2: P2/0,N0,T,Z  
#3: A,N0,T,Z  
#4: D2,N0,T,Z  
#5: D5  
#6: D3,N0 JUMP TO #1

The symbols in the sequence are in the usual Nicolet/GE language; our addition of "Z" institutes homo-mode decoupling (the hardware switch is left on hetero). Combining "Z" with "T" also allows one to do the hetero saturation and homo decoupling at different decoupler power levels. A simple example of the utility of this capability is shown in the figure using the TMS + ethylbenzene standard sample. The lower trace is the normal spectrum; the

upper trace shows saturation of the TMS line and homonuclear decoupling of the quartet leading to collapse of the triplet.

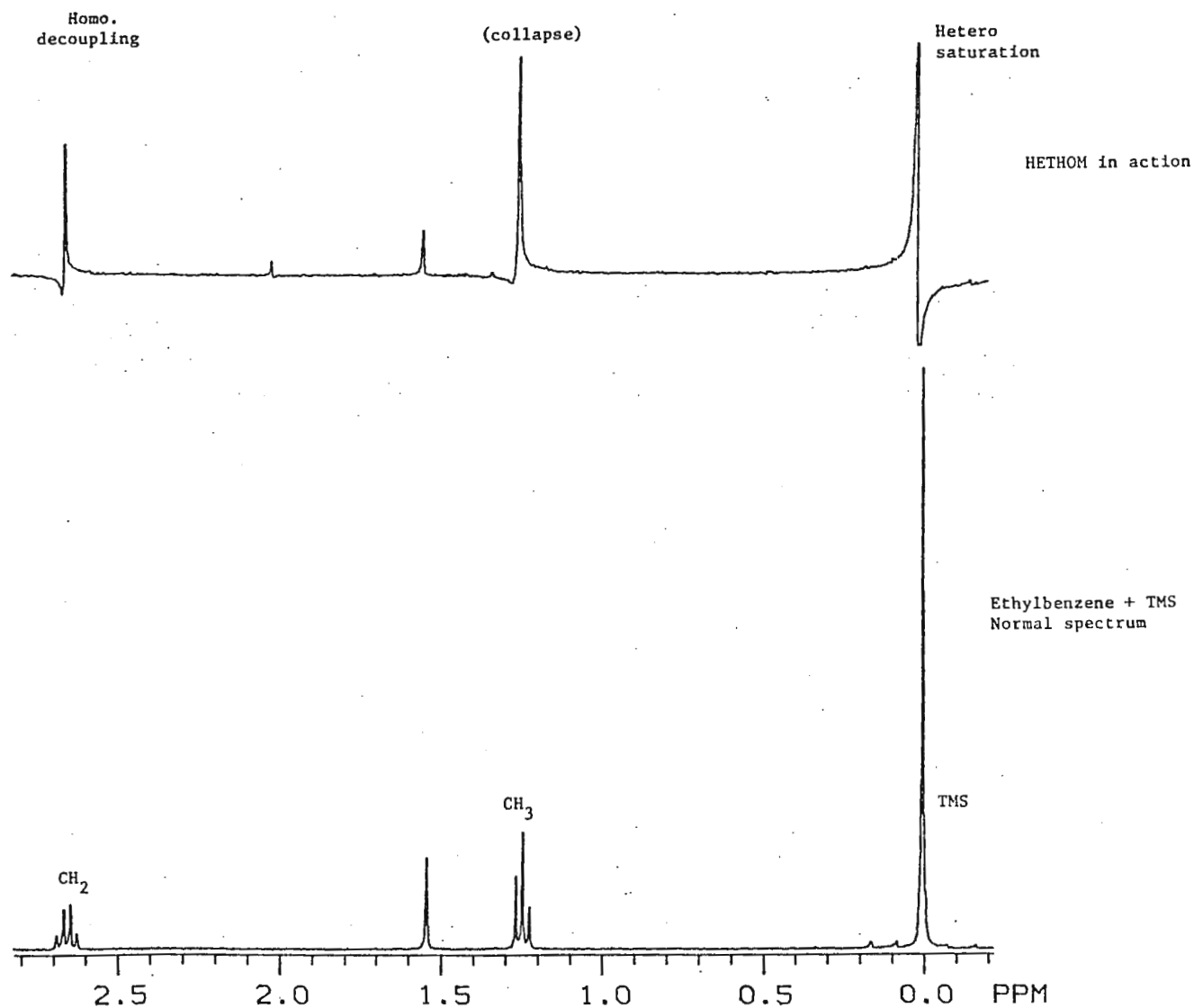
Please credit this to Professor G. N. LaMar's subscription.

Sincerely,

Jeff  
Jeffrey J. de Ropp

Steven W. Unger  
Steven W. Unger

JSdR/SU/dd



# Mobil Research and Development Corporation

March 24, 1986

RESEARCH DEPARTMENT  
DALLAS RESEARCH LABORATORY  
P.O. BOX 819047  
DALLAS, TEXAS 75381-9047

13777 MIDWAY ROAD  
DALLAS, TEXAS 75244-4312

EUGENE L. JONES  
MANAGER

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

**Subject: High Speed Spinning for Al-27 MAS NMR at 6.35 Tesla**

Dear Barry:

We are interested in using aluminum-27 MAS NMR to analyze clay materials. Such clays typically have a large octahedrally coordinated aluminum peak near 0 ppm and a smaller tetrahedrally coordinated peak near 70 ppm. Because of the second-order nuclear electric quadrupolar broadening, the NMR lines tend to be broad at our low magnetic field of 6.35 Tesla. Hence, the first spinning sideband from the octahedral aluminum seriously interferes with the center band of the tetrahedral aluminum at the ordinary spinning speeds of 4.0 - 5.5 kHz (57 - 78 ppm).

This interference has been greatly reduced with the recent installation of our Chemagnetics high speed CP/MAS probe. We have made a number of measurements on clays at approximately 8.9 kHz (127 ppm) spinning speed. Figure 1 shows an example. The clay is Madison illite, which had been obtained from Dr. John Hower. Note the nearby complete removal of the spinning sidebands from the center bands. The ability to determine tetrahedral versus octahedral aluminum is greatly increased at this high spinning speed.

Although this high speed spinning greatly improves the performance of low-field systems for MAS of quadrupolar nuclei, it is not an effective substitute for high-field spectrometers. This is because the increase in field greatly decreases the line widths and increases resolution. A "dream machine" for aluminum would have a 14.1 Tesla magnet and a one mega-rpm spinner; I believe this is possible.

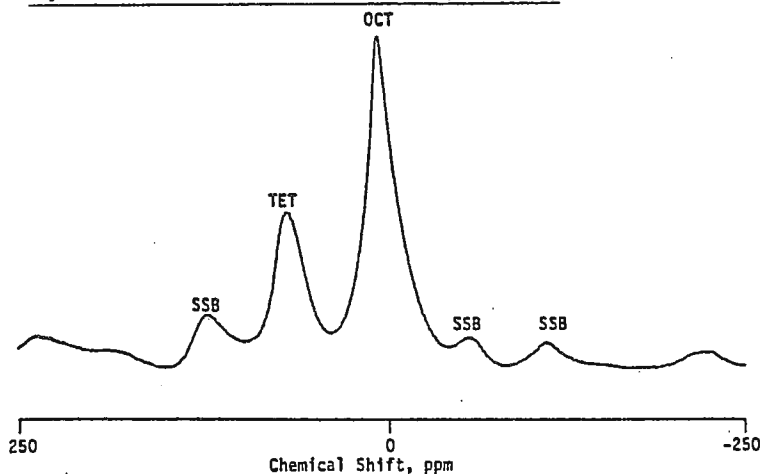
Sincerely,



D. E. Woessner

DEW:dpj  
Attachment

Figure 1. Al-27 MAS NMR of Madison Illite (70.286 MHz)



R.L. Wershaw  
Water Resources Division  
Mail Stop 407  
Box 25046  
Denver Federal Center  
Denver, CO 80226

#### SYMPOSIUM NOTICE

June 8 and 9, 1986

ACS-8th Rocky Mountain Regional Meeting  
Denver, Colorado

"PROBLEMS AND SOLUTIONS TO THE APPLICATION OF MAGNETIC RESONANCE  
IN THE STUDY OF HUMIC SUBSTANCES AND OTHER COMPLEX GEOLOGICAL  
MATERIALS."

#### List of Invited Speakers

- Robert L. Wershaw (USGS) & M. A. Mikita (Univ. of Colo.). Introduction and scope of the problems.
- Caroline Preston (Agriculture, Canada). Review of solution NMR spectroscopy of humic substances.
- Gary Maciel & James Frye (NSF Regional NMR Center, Colo. State Univ.). Review of solid state NMR spectroscopy of humic substances.
- Cornelius Steelink (Univ. of Ariz.). Review of electron spin resonance spectroscopy of humic substances.
- Michael Mikita (Univ. of Colo.). The chemistry and spectral applications of derivatization techniques for humic substances.
- Larry Dennis (Exxon Research and Eng. Co.). Polarization transfer and 2-D experiments in solution spectroscopy of humic materials and synthetic fuel liquids.
- Eiichi Fukushima (Lovelace Research Foundation). Techniques employed in the measurement of wide-line NMR spectra.
- Stephen Smallcomb (Varian Instrument Div.). Design and limitations of liquid-state NMR spectrometers.
- Robert L. Wershaw (USGS). NMR evidence for the membrane model of humic substances.
- William Earl (Los Alamos Natl. Lab.). Detection of mobile phases in the solid-state NMR spectra of model systems.
- David E. Grant (Univ. of Utah). Carbon-13 chemical shift anisotropies from single crystal pyrene.
- David E. Axelson (Energy, Mines and Resources, Canada). Detection of mobile phases in the solid-state NMR spectra of coals.
- Tony Vassallo (Commonwealth Scientific and Industrial Research Organization). Quantitative reliability in the solid-state NMR spectra of humic substances.
- Michael A. Mikita (Univ. of Colo.) & R. L. Wershaw (USGS). Summary and recommendations.

The Proceedings of this Symposium will be Published.



McMASTER UNIVERSITY

Department of Chemistry

1280 Main Street West, Hamilton, Ontario, L8S 4M1

Telephone: 525-9140

February 26, 1986

Professor B. L. Shapiro  
Texas A & M University  
College Station  
Texas 77843  
U.S.A.

Dear Barry:

## Geminal Deuterium Isotope Effects on Deuterium Chemical Shifts

We have recently installed a Bruker AM500 in our NMR facility and the performance of the new Bruker magnets is impressive. There are currently two 500 MHz instruments operational in Canada, the one at McMaster being the only one in a University environment. We will also be installing a Bruker MSL 100 very shortly. A limited number of positions are available (P.D.F.'s etc.) and inquiries should be addressed to Dr. T. Birchall.

Deuterium magnetic resonance becomes very practical at higher fields and one of our interests is determining the amount of deuterium incorporation at various sites within a molecule. Figure 1 shows the spectrum of partially deuterated fenchone. The signals at the lower frequencies of the two pairs are due to fenchone with two deuterons at C-6 and the two signals at the higher frequencies are due to fenchone with one deuteron at C-6. The isotope shifts for exo D and endo D are 0.019 ppm and 0.021 ppm respectively. A fuller account will appear in Can. J. Chem.

N. H. Werstiuk

B. G. Sayer

G. Timmins

BGS:cd

Please credit this communication to the account of J. L. A. Thompson.

(continued on page 29)

# The NMR evolution continues:



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*NMR systems designed to solve problems.*

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(continued from page 26)

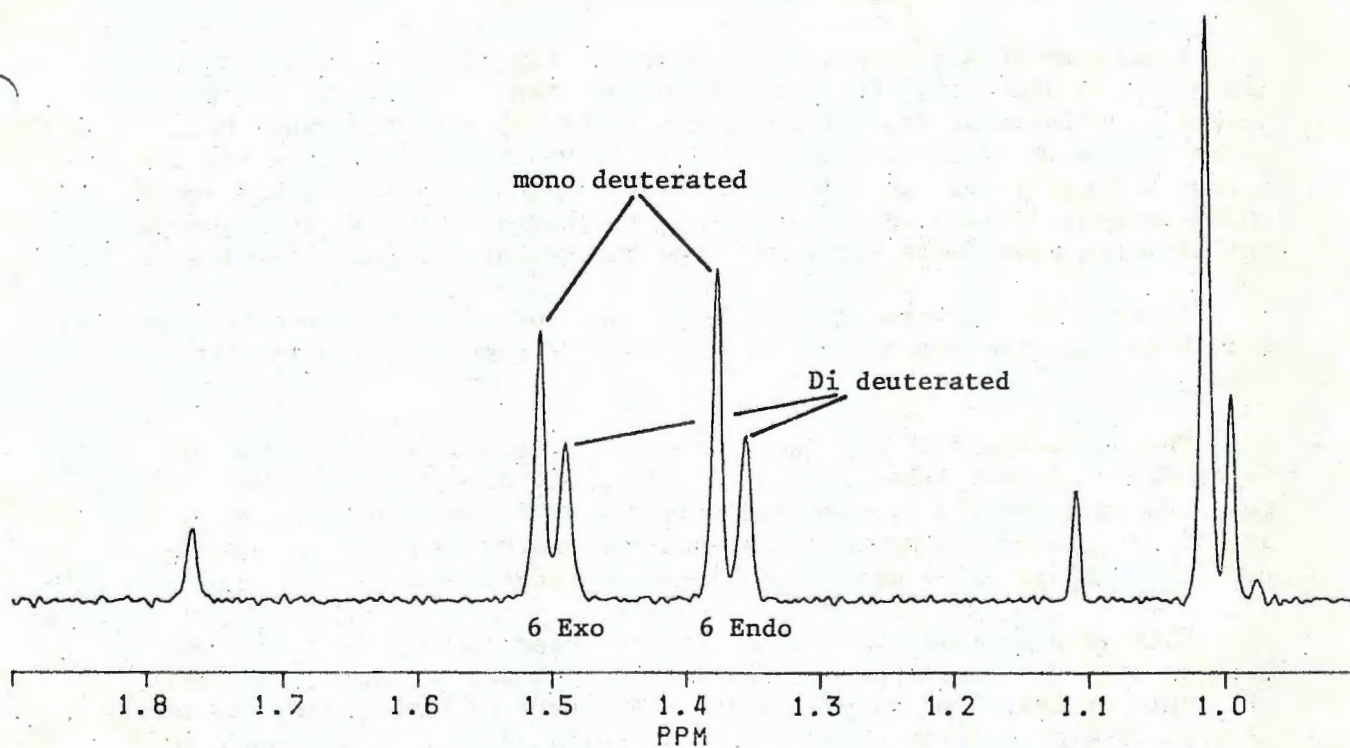
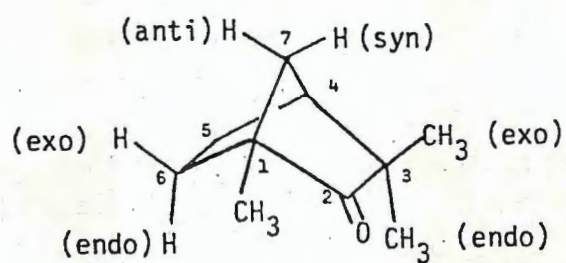


Fig. 1 76.8 MHz Deuterium Spectrum of Partially Deuterated Fenchone



THE  
UNIVERSITY  
OF  
ILLINOIS  
AT  
CHICAGO

Department of Physiology and Biophysics (M/C 901)  
Box 6998, Chicago, Illinois 60680  
(312) 996-7620

March 3, 1986

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

Simple and Efficient Apparatus  
for NMR Measurements Below 300K.

Dear Professor Shapiro:

We would like to present a very simple and economical method for cooling the sample during NMR measurements. It is based on liquid N<sub>2</sub> boil-off method, but is quite different from what one sees in many NMR laboratories. Usually, a large (about 1000 W) heater is immersed in the liquid N<sub>2</sub>, and nitrogen vapor from above the liquid level is directed to the NMR probehead.

A diagram of our apparatus is given in Figure 1. A copper tube (A) of 12 mm diameter, and a little longer than the depth of the Dewar vessel, is closed at the bottom with a plate (B) having a small hole (1 mm in diameter) at the center. Just above the hole, inside the tube, a tiny heater is mounted. It is a spiral (5 mm in diameter, and about 20 mm in length) made out of any type of resistance wire. The tube is put into the Dewar with liquid N<sub>2</sub>, and the top of the Dewar is closed.

It is worth noticing that we must keep the N<sub>2</sub> vapor pressure high enough to blow the gaseous N<sub>2</sub> through the NMR probehead (inside the tube).

The performance of such an apparatus is much better than the performance of one with the large heater immersed directly in liquid nitrogen. We have used 25 l Dewar and this was sufficient to keep the sample at 250 K for about 24 hours. The apparatus works properly as long as the liquid N<sub>2</sub> level is about 3 cm above the Dewar bottom.

With good thermal insulation of the outer tubing, we have been able to cool the sample down to 85 K. In such measurements, 25 liters of liquid N<sub>2</sub> lasts for about 5 hours. The more sophisticated version of this apparatus (with the needle-type valve instead of the small hole at the bottom, and with the heating current controlled through the feedback from the thermocouple mounted in NMR probehead) gives about 50% higher efficiency.

The apparatus was constructed at the Research Resources Center of the University of Illinois at Chicago.

Yours sincerely,

*Daniel Fiat*      *R. Goc*

Dr. Daniel Fiat and Dr. Roman Goc

RG:vr

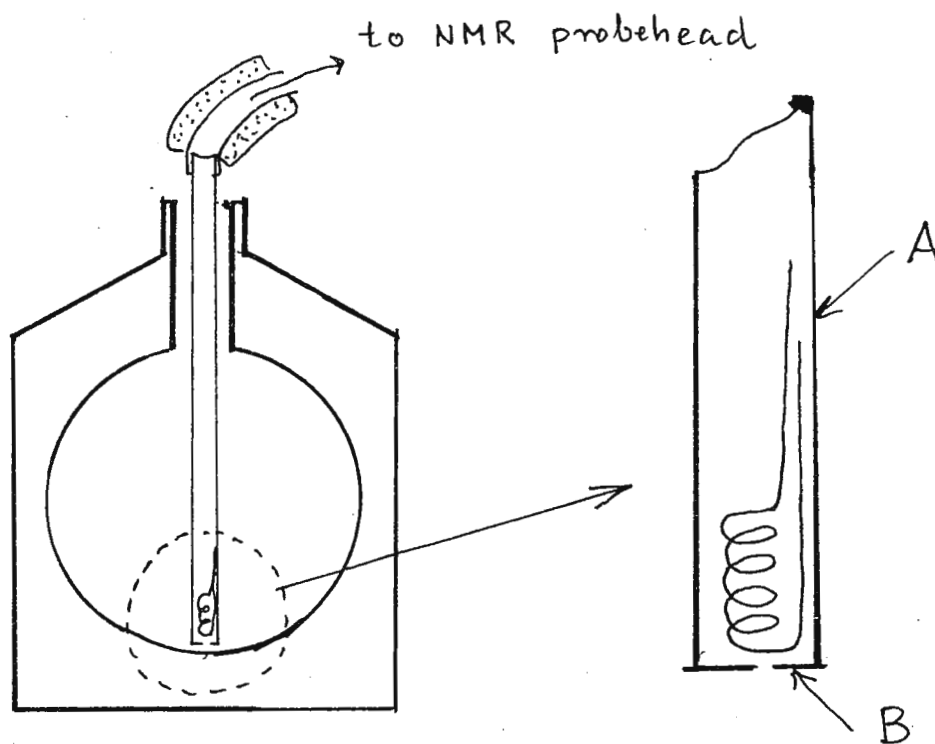


Fig. 1

UNIVERSITY OF CALIFORNIA, SAN DIEGO

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SANTA BARBARA • SANTA CRUZ

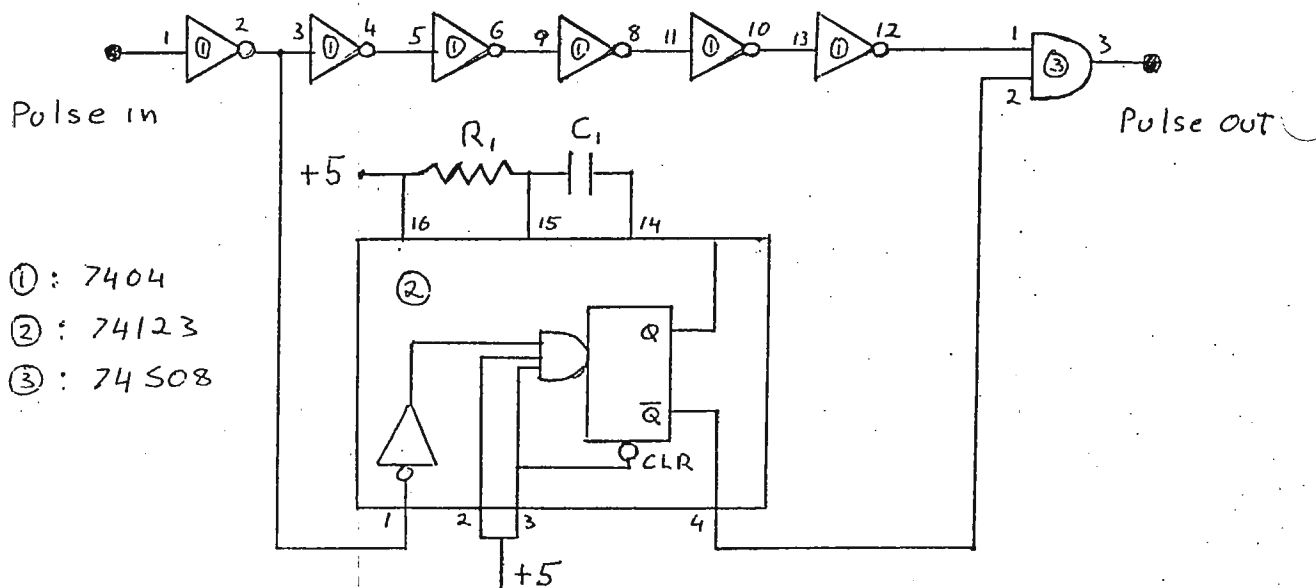
March 5, 1986

DEPARTMENT OF CHEMISTRY, B-014  
LA JOLLA, CALIFORNIA 92093Dr. Barry L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, TX 77843

## How To Keep a Wild Pulser Under Control

Dear Barry,

With most commercially available pulsed NMR software, it is all too easy to enter a pulse width in units of milliseconds or seconds instead of microseconds. Computer hardware has also been known to fail in this manner, and precious samples as well as probe/power amplifier circuitry are understandably sensitive about long, kilowatt pulses. The following circuit, inserted between the pulse programmer gate output and the rf gate input, effectively limits the maximum pulse width no matter what the computer says.



The input pulse is inverted and used to fire a retriggerable one-shot, the output of which is anded with the original pulse, slightly delayed by a string of inverters so as to avoid shortening the pulse by the propagation delay of the one-shot. Since the delay is critical to proper operation of the circuit, faster parts such as a 74S04, 74H04 or 74LS04 should not be substituted for the 7404. The pulse length limit is determined by  $R_1$  and  $C_1$ : 2k ohms and 0.1 microfarad results in a limit of approximately 50 microseconds. Since the one-shot is retriggerable an arbitrary number of pulses of legal length may be fired consecutively.

Sincerely,

Alan D. Ronemus

Robert L. Vold  
Regitze R. Vold  
Professors of Chemistry

STATION DE RECHERCHES SUR LA VIANDE



Professor B.L. SHAPIRO  
Department of Chemistry  
College Station, Texas 77843-3255  
USA

Références à rappeler :

THEIX, 1e 20 Mars 1986

NMR and Malignant hyperthermia

Dear Dr. SHAPIRO,

In humans, malignant hyperthermia constitutes a severe complication of general anaesthesia. Some strains of pigs exhibit similar and possibly identical incidents. They may serve as animal models for this disease. Contraction and metabolism traits in skeletal muscle biopsies from halothane positive pigs are studied by high resolution NMR. In a first study the water protons transverse relaxation times were measured -at low frequency- during aging biopsied muscle.

Muscle biopsies were taken from different muscles of halothane negative and halothane positive animals at different age. The factorial discriminant analysis based on NMR parameters pointed out that the age of the animals and the muscle type are very important variation factors. They have to be taken into account for halothane positive discrimination.

We are carrying on this study on a new MSL 300 delivered in november and located in the "Centre Regional de Mesures Physiques de CLERMONT FERRAND".

Sincerely yours.

Ph. GATELLIER

A handwritten signature in dark ink, appearing to be "Ph. GATELLIER", written over a horizontal line.

J.P. RENOU

A handwritten signature in dark ink, appearing to be "J.P. RENOU", written over a horizontal line.



# PHILIP MORRIS

U.S.A.

RESEARCH CENTER: P.O. BOX 26583, RICHMOND, VIRGINIA 23261-6583 TELEPHONE (804) 274-2000

March 7, 1986

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

Dear Barry:

## $^1\text{H}$ $T_1$ Discrimination in Cellulose by $^{13}\text{C}$ CP/MAS NMR

$^{13}\text{C}$  CP/MAS NMR may be used to discriminate between different domains in heterogeneous solids by inverting the proton spins and allowing them to partially recover before cross polarization to the carbons. If the proton  $T_1$ 's of the domains are different, then a delay time can be chosen so that one of the domains is nulled out. In some materials the  $T_1$ 's in the different domains may be fortuitously the same or spin diffusion may act to equalize them, making the discrimination experiment difficult or impossible. One such example is cellulose. Recently, however, I have found that by judiciously choosing the delay time, the crystalline and amorphous components of cellulose can be detected separately by this method as shown in Figures A & B. The spectra are very noisy because they were collected at delay times very close to the proton null point of both domains and the sensitivity is consequently very bad. There are perhaps better ways of selectively detecting the crystalline component such as  $T_{1\rho}$ ,  $T_{1\rho}$ , and spin exchange experiments, but these results are interesting nonetheless because they demonstrates a small but significant difference in the proton  $T_1$ 's in the two domains.

Sincerely,

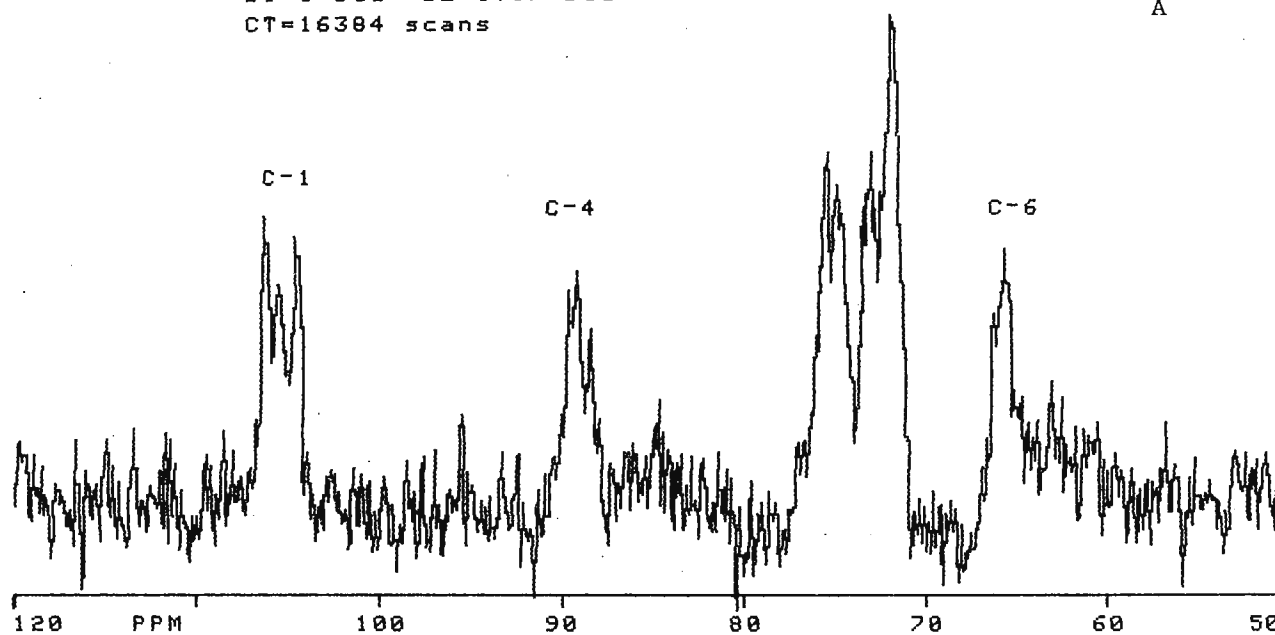
*Jan Wooten*

Jan B. Wooten .

Attachment

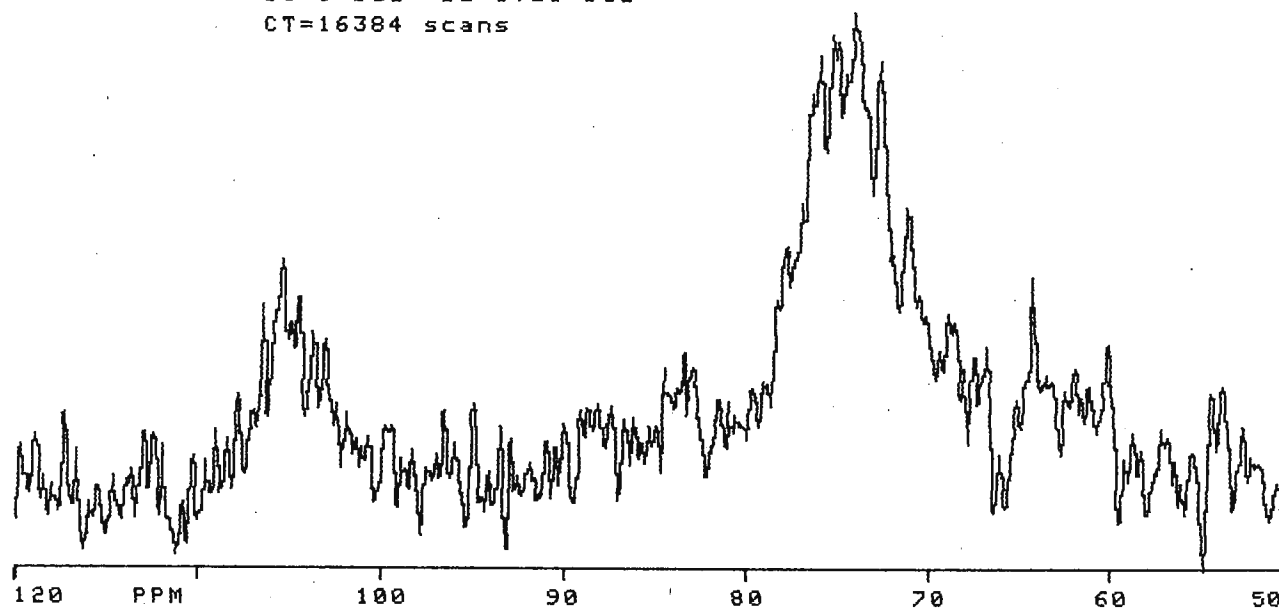
Cotton Linters  
13C CP/MAS with 1H inversion C-2,3,5  
D1=5 sec D2=0.17 sec  
CT=16384 scans

A



Cotton linters  
13C CP/MAS with 1H inversion  
D1=5 sec D2=0.25 sec  
CT=16384 scans

B



Pulse sequence: D1-P180-D2-P90-CP-Decouple (1H)  
D1-----D2-----CP-AT (13C)



## DUKE UNIVERSITY MEDICAL CENTER

Department of Radiology

25 March 1986

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

Re: Induced  $^{23}\text{Na}$  Signal Behavior

Dear Professor Shapiro:

We have recently studied the induced chemical shift and relaxation behavior of the  $^{23}\text{Na}$  signal in the presence of  $\text{Dy}^{3+}$  and  $\text{Gd}^{3+}$  chelates. The figure shows inversion recovery spectra at a fixed value of delay time (composite  $\pi - \tau - \pi/2$ ;  $\tau = 0.015\text{s}$ ) for NaCl solutions at pH 7.4 in coaxial tubes, with the inner tube containing NaCl (0.15M) and Tris-HCl buffer (0.01 M) and the outer tube containing the same components plus lanthanide metal chelate (0.01M). Each spectrum (A-F) shows two distinct chemically shifted  $^{23}\text{Na}$  resonances. The resonance from lanthanide-free 150 mM NaCl reference standard in the inner coaxial tube is set at 0 ppm. The second signal in each spectrum arises from the  $\text{Na}^+$  in the presence of lanthanide salts in the annular space between the inner and outer tubes.

The  $\text{Dy}(\text{TPP})_2$  complex induces a particularly large highfield shift of 14 ppm (spectrum C) as previously reported.<sup>1</sup> However, the  $\text{Dy}(\text{EDTA})$  and  $\text{Dy}(\text{DTPA})$  complexes produce only moderate lowfield shifts (spectra A and B). Surprisingly, all three Gd complexes induce moderate 1-2 ppm lowfield shifts (spectra D-F). The data also reveal that at similar concentrations (0.010M), the  $\text{Gd}(\text{DTPA})$  complex actually induces a larger lowfield shift than the  $\text{Dy}(\text{DTPA})$  complex.

Comparison of our measured  $T_1$  and  $T_2$  values with control NaCl solutions reveals that the relaxation behavior of the  $^{23}\text{Na}$  signals is independent of buffer and ions, other than the added lanthanide. From the partially-relaxed spectra, it is readily apparent that the Gd complexes are more effective than the corresponding Dy complexes at inducing  $^{23}\text{Na}$  relaxation, and that the EDTA and DTPA complexes are less efficient than the TPP complex. Another interesting observation is that the most effective shift reagent,  $\text{Dy}(\text{TPP})_2$ , is also a very good relaxation agent being more effective than either  $\text{Gd}(\text{EDTA})$  or  $\text{Gd}(\text{DTPA})$ .

Induced sodium shifts of the 1-2 ppm magnitude with Gd complexes have not previously been reported.<sup>2,3</sup> This discovery is significant since Gd complexes have generally been used as relaxation agents, and the  $\text{Gd}(\text{DTPA})$  complex is currently undergoing clinical trials as a magnetic resonance imaging contrast

(continued on page 39)



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C

2

12

C

2

2

C

(continued from page 36)

agent. With the added potential for in vivo differentiation of intracellular from extracellular  $\text{Na}^+$ , this biocompatible compound may be equally useful for in vivo spectroscopy.

Sincerely,

*M. A. Brown*

M. A. Brown

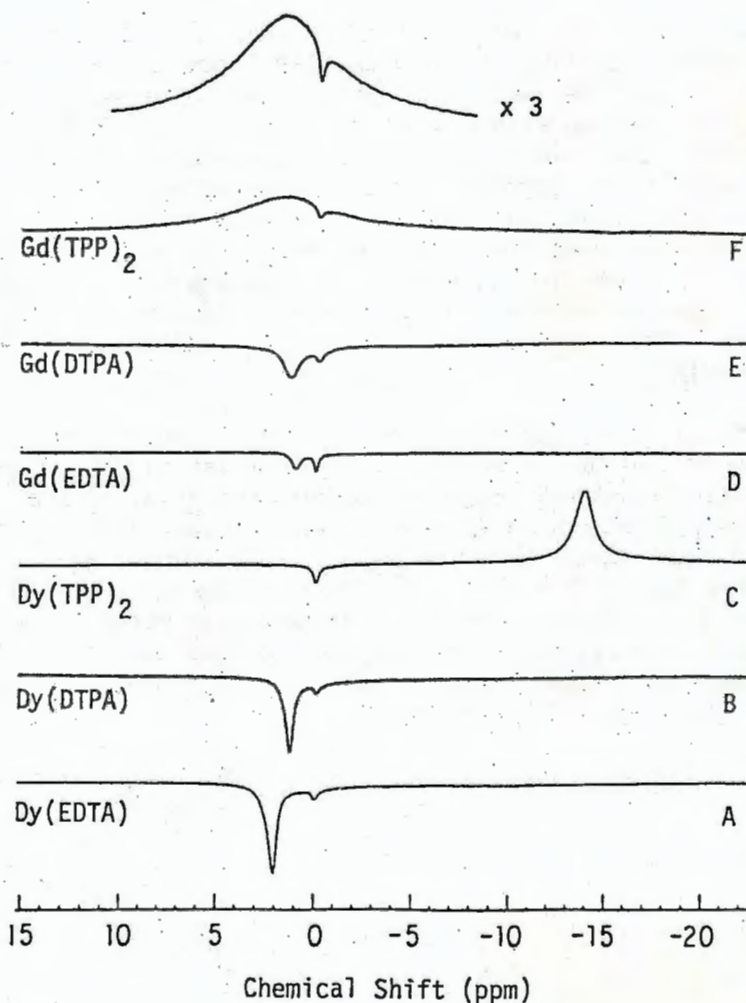
*Tony Ribeiro*

A. A. Ribeiro

*Len Spicer*

L. D. Spicer

1. R.K. Gupta and P. Gupta, J. Magn. Reson. 47, 344 (1982).
2. A preliminary report of a 0.14 ppm sodium shift measured in perfused rat hearts with Gd(EDTA) has been reported (Malloy, et al., 22nd ENC, Asilomar, CA, 1981).
3. Dipolar shifts of 0.2 ppm have been reported for three Gd complexes (Bryden et al., Anal. Chem. 53, 1418-1425, 1981).





## UNIVERSITY OF SOUTH CAROLINA

COLUMBIA, S. C. 29208

SOUTH CAROLINA MAGNETIC  
RESONANCE LABORATORY

(803) 777 7341

March 11, 1986

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

Product Operator and Density Matrix Calculations With Computer Algebra

Dear Barry:

In the past few years we've been playing with computer algebra (CA) in our lab. Our mainframe Vax 11/780 runs SMP,<sup>1</sup> one of the newer CA languages. Until recently we used SMP mainly to carry out coordinate transformations and powder averages involving Wigner rotation matrices. However, about 9 months ago one of us (AJB) began using it in spin gymnastics calculations (neglecting relaxation) based on the product operator formalism.<sup>2</sup> In its present form, the program can only deal with up to two weakly coupled spin 1/2 nuclei, but it is nevertheless a powerful tool for analyzing and developing complicated pulse sequences. Perhaps more importantly, interactive spin gymnastics "play-sessions" are a fantastic way to learn what is going on in more advanced NMR pulse sequences. Extension of the program to handle up to 4 weakly coupled spins is forthcoming.

Unlike the product operator program, the density matrix methods which AJB has developed<sup>3</sup> are not limited to a small set of weakly-coupled spin 1/2 nuclei. Furthermore, these programming methods will be published shortly so that NMR spectroscopists will have free access to them. To date, we have successfully applied these methods to the following cases: a strong (Dirac delta) pulse to a spin 1/2 nucleus, a strong pulse to a spin 1 nucleus, a weak pulse of finite duration to a spin 1/2 nucleus, a strong pulse to two weakly coupled spin 1/2 nuclei, a strong pulse to two strongly coupled spin 1/2 nuclei, the quadecho pulse sequence for a spin 1 nucleus, and the quadecho pulse sequence for a spin 3/2 nucleus.

Beyond the pedagogical reasons, the value of these CA density matrix and product operator calculations lies in the analytical results they provide. For a given pulse sequence and a given spin system, one can generate an analytical expression for the observable signal at the first moment of acquisition or as a function of the acquisition time. Fourier transformation of the latter gives an analytical stick spectrum. If there is a second evolution time in the sequence, a 2D stick spectrum is obtained. Also, if one has the analytical expression for the signal in terms of all pertinent NMR parameters, one can clearly choose numerical values for the parameters such that the desired signal intensity is maximized. Thus, in the analytical result for the spin 1 quadecho pulse sequence, we confirm that the maximum echo signal along the imaginary (y) axis is obtained if the flip angle of the second pulse is  $\pi/2$  and its phase is shifted by  $\pi/2$  relative to the first  $\pi/2$  pulse.

Yours truly,



Alan J. Benesi, Manager  
South Carolina Magnetic Resonance Lab



Paul D. Ellis  
George H. Bunch, Sr., Professor  
of Chemistry and Facility Director

AJB&PDE/wg

#### References

1. Inference Corporation, Computer Mathematics Groups, 5300 W. Century Blvd., Los Angeles, CA 90045.
2. O.W. Sorensen, G.W. Eich, M.H. Levitt, G. Bodenhausen, and R.R. Ernst, Prog. in NMR Spectroscopy, 16, pp. 163-192 (1983).
3. A.J. Benesi, T.E. Raidy, and P. D. Ellis, J. Mag. Res., submitted.



## DEPARTMENT OF HEALTH &amp; HUMAN SERVICES

Public Health Service

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

National Institutes of Health  
 Bethesda, Maryland 20205  
 Building : 13  
 Room : 3W-13  
 (301) 496-5771  
 Mar. 20, 1986

*Double Vision - Figuratively Speaking*

Dear Barry,

In the course of teaching about imaging techniques, we have found that the impact of figures which attempt to portray three dimensions (e.g. rotating frame vectors, quadrature f.i.d.'s etc.) is enormously enhanced when simple stereoscopic techniques are used. Using either a cheap pair of lenses (or if you have the ability, decoupling by relaxation one's ocular muscles) to view the figures we have drawn, we think the point is made. (In extremis, cross your eyes, then slowly relax them until the four images become three. The center image is 3D, but with the perspective 180° reversed !) Producing the images with a computer is trivial. The trick is that when viewing objects close to you, your eyes turn in, thus those objects must be closer together in the two displays. So if you are viewing a scene so that the x axis of a coordinate system runs toward you while the y axis lies parallel to the horizon and the z axis is vertical, the drawing paper X and Y coordinates of the two plots are

$$X_{\text{left}} = -\beta + y(1 + x/r) + \beta x/r$$

$$X_{\text{right}} = \beta + y(1 + x/r) - \beta x/r$$

$$Y = z(1 + x/r)$$

where (x,y,z) are the coordinates of the point of interest, and  $2\beta$  is the distance between the two origins. In a final publication  $\beta$  should be about 2.5 cms as shown here, though we usually double the size for manuscripts and let the publisher photo-reduce by a factor of two. r is the distance of the viewer from the scene and for objects lying with a spherical volume 10 cms in diameter (thus  $\beta = 5\text{cms}$ ) we usually view from about  $r=45\text{ cms}$ . Of course, with a three dimensional object you also have to decide upon your

perspective, and some views give better stereo pictures than others. There is also a small amount of training of your eyes involved, but we feel that the subjective impact of such displays merits the minor inconvenience to the writer, publisher and reader.

Please credit this contribution to Dr. E.D. Becker's account.

With best wishes.

Yours sincerely,

*D. I. Hoult /cnc*

D.I.Hoult

*C.N. Chen*

C-N. Chen

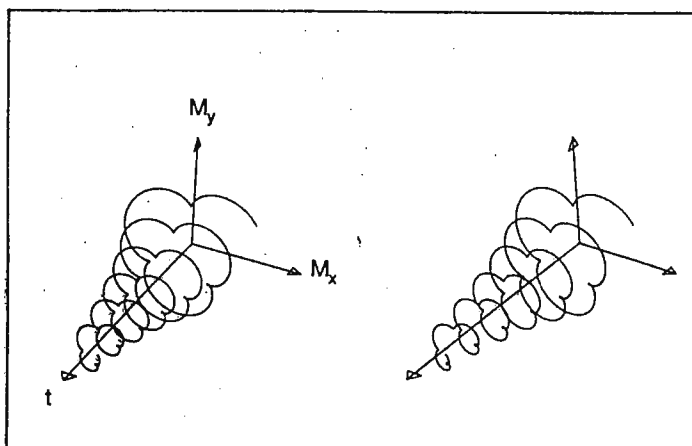


Fig.1

Stereo pair of magnetization  $M_x$ ,  $M_y$  plot against time,  $t$ . The f.i.d. is composed of two frequency components.

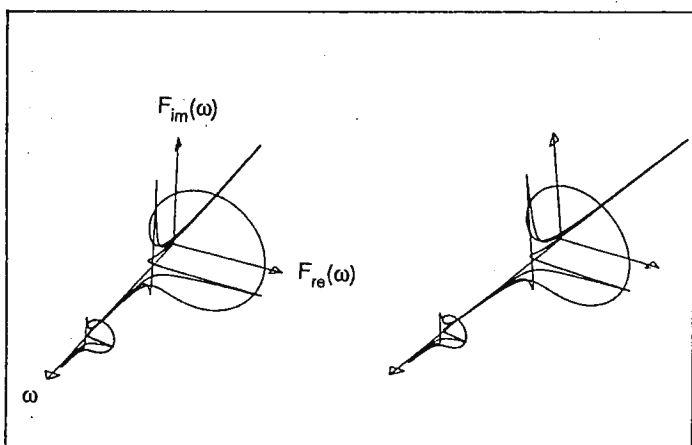


Fig.2

The same signal as above, but plot in the frequency domain. The projections of the trajectory (the one with two fancy loops) onto the  $F_{re}(\omega)$ - $\omega$  and  $F_{im}(\omega)$ - $\omega$  planes are the real and the imaginary part, respectively, seen in a conventional spectrum.



UNIVERSITY OF MISSOURI-COLUMBIA

March 21, 1986

College of Arts and Science

Department of Chemistry

 123 Chemistry Building  
 Columbia, Missouri 65211  
 Telephone (314) 882-2439

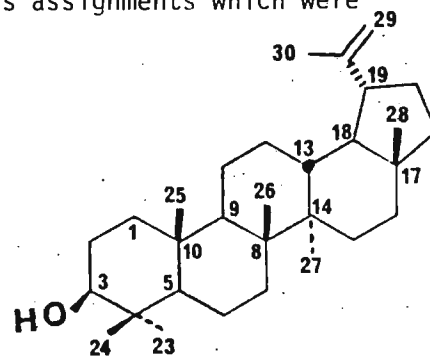
Professor Bernard L. Shapiro  
 Department of Chemistry  
 Texas A&M University  
 College Station, TX 77843

### $^{13}\text{C}$ NMR Assignments of Lupeol by Autocorrelated 2D DQC Spectroscopy

Dear Professor Shapiro:

The assignment of NMR spectra of natural products is commonly based on comparison to related compounds in a series and are often not unambiguous. One of our graduate students, Rattanaorn Promsattha, recently isolated 500 mg of the pentacyclic triterpene lupeol which has been used as a model for the assignment of a series of related compounds.<sup>1</sup> This proved a good opportunity to try Turner's 2-D autocorrelated double quantum coherence experiment<sup>2</sup> to unambiguously confirm the previous assignments which were based on traditional 1-D methods.<sup>1</sup>

The experiment was performed in the 5mm probe of our NT-300 WB in 43 hours on a saturated solution in  $\text{CDCl}_3$ . A total of 28  $^{13}\text{C}$ - $^{13}\text{C}$  correlations were observed allowing complete assignment of the C-13 spectrum from this experiment alone. An expanded portion of the 2-D plot is shown in the figure together with the 1-D spectrum and assignments.



Lupeol

It is a tribute to Wenkert, et al., that these results are in complete agreement with their carbon assignments<sup>1</sup> made in 1978.

Please, credit this contribution to Tuck C. Wong's account.

Sincerely,

Michael S. Tempesta  
 Assistant Professor  
 of Chemistry

Richard B. Taylor  
 NMR Spectroscopist

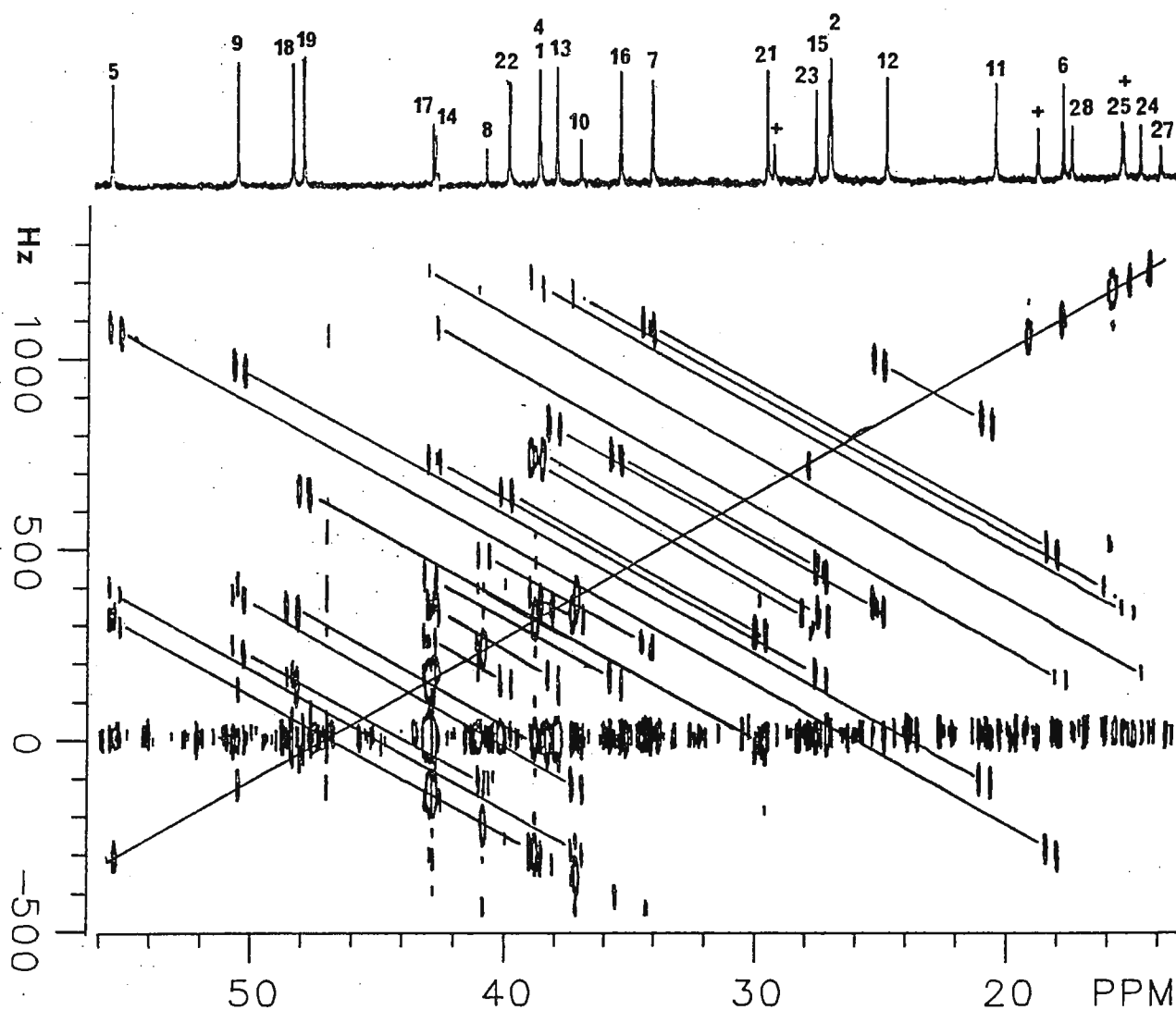


Figure 1.  $^{13}\text{C}$  autocorrelated 2D-DQC spectrum of Lupeol with the 1-D spectrum and assignments above. + Peaks due to impurities.

1. E. Wenkert, G.V. Baddeley, I.R. Burfitt and L.N. Moreno, *Org. Magn. Reson.* 11, 337(1978).
2. D.L. Turner, *Molec. Phys.* 44, 1051(1981); D.L. Turner, *J. Magn. Reson.* 49, 175(1982); D.L. Turner, *J. Magn. Reson.* 53, 259(1983).



University of Alberta  
Edmonton

Canada T6G 2G2

Department of Chemistry  
Faculty of Science

E3-43 Chemistry Building East, Telephone (403) 432-3254

February 20, 1986

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

Re: Diablo Drive Compatibility

Dear Barry:

Owners of older computer systems using the Series 30 Diablo Disc Drives may experience problems when swapping disc cartridges among several drives. Error messages such as "Bad Disc", "Corrupt Directory", "S108" (Bruker systems), etc., can be very frustrating when they disappear on using a different drive.

In our experience, most such problems result from incompatibilities in the Sector Timing adjustment. Using the special Alignment Cartridge, this is supposed to be set to 30  $\mu$ s; however, adjusting our six drives (on three computers) to this value only made the problem worse. In passing, it might be noted that there doesn't seem to be anything sacred about the 30  $\mu$ s value; drives adjusted to anywhere from 5  $\mu$ s to 55  $\mu$ s performed quite happily on their own.

Our solution, in the end, requires no special tools and may even be done without the use of the Alignment Cartridge. We choose one drive as a reference (the most reliable, most heavily used, etc.), and record a known number pattern on a disc with this drive (Bruker DSKTST #4). The disc is transferred to another drive and while the number pattern is being read (DSKTST #0 or #6) the sector timing screw is adjusted first CW (shorter times) until READ ERRORS just begin, then CCW until READ ERRORS just begin, and then halfway back to CW limit. The range of this adjustment is about 360° (CW to CCW) corresponding to about 45  $\mu$ s. A further decrease of 5  $\mu$ s (CW 45°) should then be made. We found it useful to place a crude goniometer on the shaft of the screwdriver (a small square of cardboard with lines ruled every 45°) as an aid in quantifying the adjustment.

Using this method, our reference drive has a sector timing of 35  $\mu$ s and our five other drives range from 29  $\mu$ s to 46  $\mu$ s and we enjoy trouble-free interchangeability among all drives.

Please credit this contribution to Tom Nakashima's subscription.

Yours sincerely,

Glen Bigam

GB:lf

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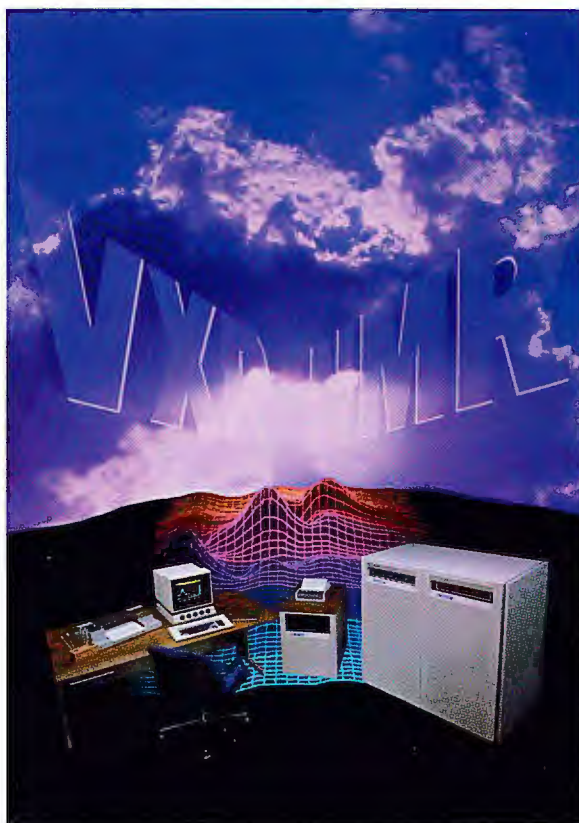
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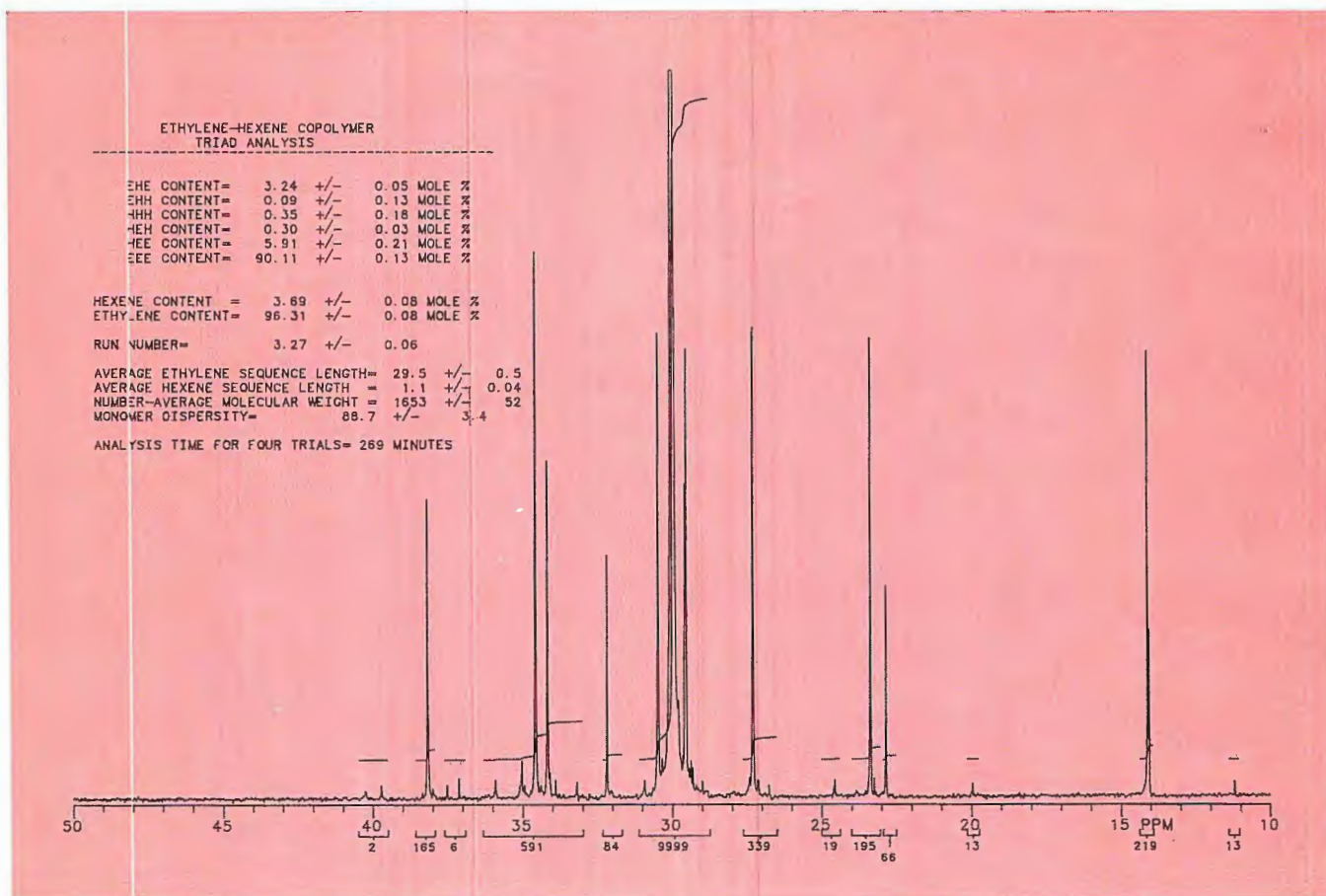
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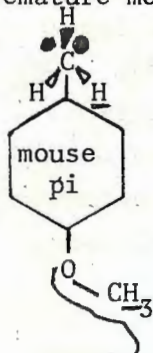
March 18, 1986

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

Dear Barry:

Head to tail communication.

Really, Barry, you know very well that the gestation period for elephants is longer than nine months! However, after such cruel treatment from you, we labored mightily and brought forth - the premature mouse you see before you. The head communicates with the



tail to the extent of 51 millihertz, but only if the tail is flaccid. If the mouse is annoyed and lifts its tail, then all communication stops. If you decapitate the mouse, then the tail still communicates with what was the head (virtual orb) to the tune of -43 millihertz, or at least so Rudy Sebastian tells me. He converses better with mice than I do. All this may annoy Adam Allerhand, who will no doubt recommend

communication via the backbone; which facilitates finer filming, as he has so cleverly shown.

Does all this also annoy you and will you nevertheless relent and restore me to a state of grace? I plan to send you a picture of the mature mouse or its shadow at Christmas, perhaps gracing a commemorative stamp, and taken with an expensive Bruker camera at three hundred hours on a cold morning.

Supplicatingly yours,

*Ted*  
Ted Schaefer.

TS/cd

# RESONANCE MAGNETIQUE NUCLEAIRE DE MATERIAUX SOLIDES

---

Montpellier, 1e March 18, 1986

$^{13}\text{C}$  MAS NMR on  
Organic Conducting Crystals

Pr. B.L. SHAPIRO  
Dept. of Chemistry  
Texas A and M University  
College Station  
Texas 77843  
U.S.A.

Dear Pr. Shapiro,

Following the high resolution  $^{13}\text{C}$  NMR work started one year ago on organic conducting crystals of the (TMTSF) X series with  $\text{X} = \text{ClO}_4$ ,  $\text{ReO}_4$  (see TAMU Newsletter n° 321), we have tried to investigate the temperature dependence of all the observed resonance shifts. The metallic system  $(\text{TMTSF})_2\text{ReO}_4$  is particularly suitable for that purpose as it experiences a structural transition at 182°K below which it becomes insulating. Performing this experiment had a double interest :

- i) to be able to define the "actual" insulating position for all the  $^{13}\text{C}$  resonances of the organic molecule (zero Knight shift),
- ii) consequently, to be able to follow the temperature variations of all the resolved  $^{13}\text{C}$  Knight shifts.

From the figure, it is clear that the four corner carbons (a) and the four methyl carbons (b) give well resolved lines at high temperature whose positions vary when T decreases. At  $\sim 182^\circ\text{K}$ , the structural transition occurs, which appears as a very deep change in the appearance of the spectra. At lower temperatures, the resonance positions are stable. An "insulator reference shift" of  $\sim +17$  ppm is reasonable for methyl carbons, but the analysis of the corner carbons case is much more delicate and all the observed resonances have not yet been attributed.

We want to emphasize the interest of this type of experiment to investigate the electronic and structural properties of organic conducting crystals.

Measurements have been made on a CXP 300 at Bruker-Karlsruhe, with an incomparable help from Martine ZILIOX (ingenior at Bruker). We have used the recent variable temperature, double bearing MAS probe.

Sincerely yours.

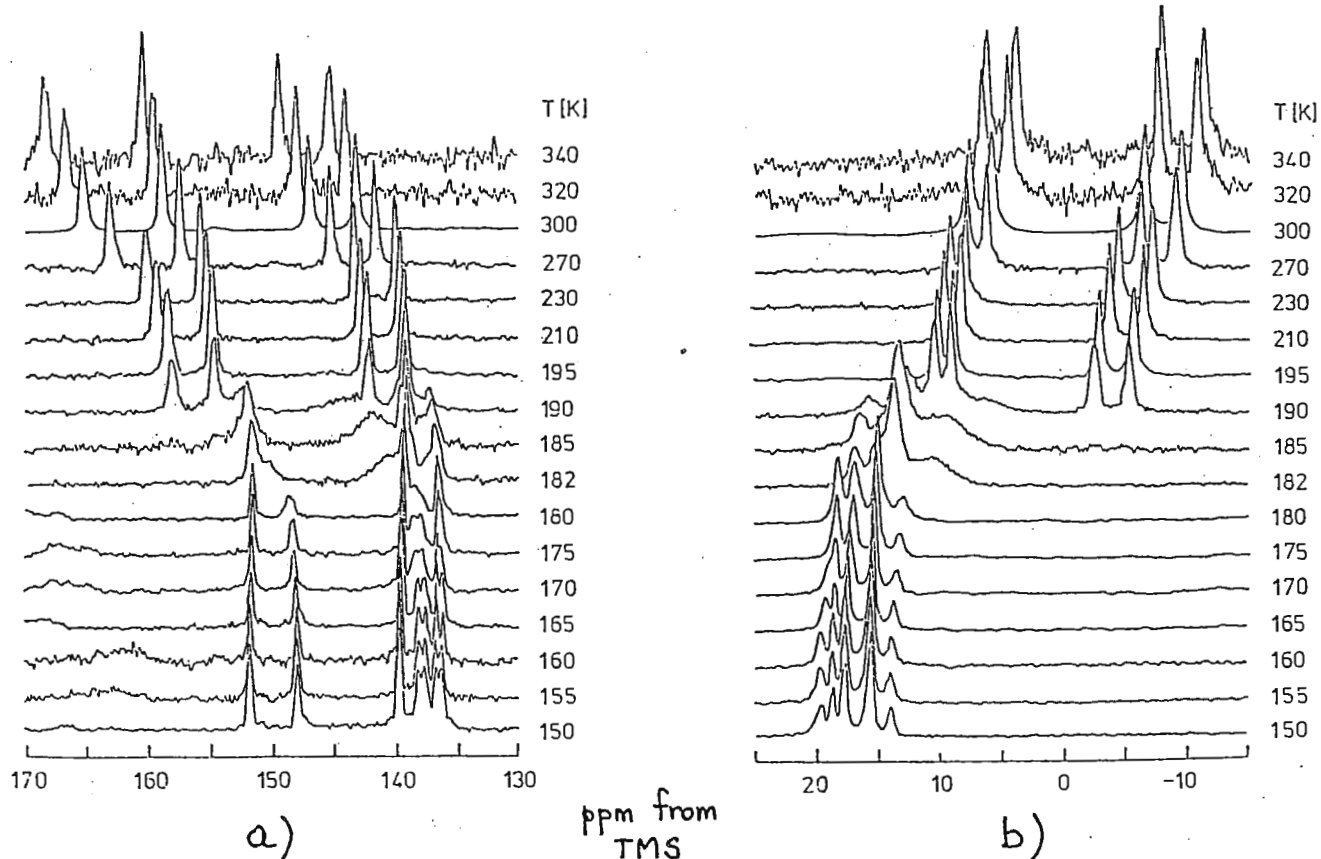
*Bernier*

P. BERNIER

*pcsk*

P.C. STEIN

# <sup>13</sup>C MAS NMR





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(317) 923-1321

March 19, 1986

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

Title: FID of an Exchange-Collapsed Doublet

Dear Barry:

Some years ago Powles and Strange, Mol. Phys. 8, 169 (1980) showed that the spin echo of an exchange-collapsed doublet showed up its original uncollapsed origin by having terms in the spin echo which would not be present for a true single line. What they did not discuss was a means to ascertain if the doublet arose from an equal concentration pair or an unequal concentration pair. I propose a very simple way to accomplish this differentiation.

After considering some complex modifications of the spin echo sequence, it dawned on me that the answer was right before my eyes. Following a  $90^\circ$  pulse about the y axis in a coordinate system rotating at the collapsed resonant frequency

$$\omega = \omega_A P_A + \omega_B P_B,$$

(where  $\omega_A$  &  $\omega_B$  are the resonance frequencies in the absence of exchange and  $P_A$  &  $P_B$  are the fractional concentrations of the two species) the magnetization along the y axis,  $M_y$ , is nonzero only if  $P_A \neq P_B$ . For a single line or for a collapsed doublet for which  $P_A = P_B$ ,  $M_y$  is exactly zero.  $M_y$  is given by

$$M_y \sim (e^{S_1^+ t} - e^{S_1^- t} \cos S_2^- t) \frac{(R_1 + S_1^-) S_2^-}{(S_1^+ - S_1^-)^2} - \frac{(S_1^- + R_1)}{(S_1^+ - S_1^-)} e^{S_1^- t} \sin S_2^- t$$

where (note  $P_A + P_B = 1$ )

$$S_1^+ = -(\omega_B - \omega_A)^2 \tau P_A^2 P_B^2 - 1/T_2$$

$$S_1^- = 1/\tau(1/P_A + 1/P_B) - (\omega_B - \omega_A)^2 \tau P_A^2 P_B^2 - 1/T_2$$

$$S_2^- = (\omega_B - \omega_A)(P_B - P_A)$$

$$R_1 = 2/\tau (P_A/P_B + P_B/P_A)$$

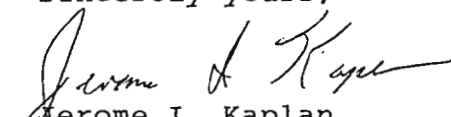
and

$$P_A/\tau_A = P_B/\tau_B = 1/\tau.$$

Note that  $M_Y(t) = 0$  for  $P_A = P_B$ .  $M_Y(t)$  rises rapidly, levels out, and then has a slow decay as determined by  $S_1$ .

Please credit this contribution to the account of B. D. Nageswara Rao.

Sincerely yours,

  
Jerome I. Kaplan  
Professor of Physics

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BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN

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

There's No Fuel Like an Old Fuel  
(title provided by the Editor)

Our reference

Your reference

Telephone  
Sunbury-on-Thames  
(09327) 6 2153

Date

S/SYB/207/86

20th March, 1986

Dear Barry

As part of our research programme aimed at understanding the structures of fossil fuels, we have recently developed a procedure for obtaining the average chemical structure from CP-MAS NMR data. By use of a standard CP-MAS spectrum and a dipolar dephased CP-MAS spectrum, a quaternary and methyl subspectrum, and a protonated carbon subspectrum are generated. These are subjected to the deconvolution procedure described below, and allows us to analyse fossil fuels in terms of specific carbon types.

The heterogeneous/multiphase nature of fossil fuels gives rise to a chemical shift dispersion, which is the dominant mechanism of line broadening at higher magnetic fields. An estimate of the distribution of shifts expected for each carbon type was made by constructing a histogram of literature chemical shifts for 140 model hydrocarbon compounds (BASF-AG data base). For deconvolution purposes, a single or double Gaussian distribution was used for each carbon type with the mean and width determined from the histograms. These Gaussian peaks were then subtracted from the experimental spectra; the intensity being the only variable parameter. At present this procedure is carried out on the Jeol FX200 computer, but in the near future we hope to be able to transfer NMR data from the FX200 to our VAX network.

We illustrate this procedure with the analysis of Green River oil shale. The spectra (Figures 1 and 2) were obtained with a contact time of 1 msec and a recycle time of 2 sec. For the dipolar dephased spectrum, the decoupler was gated off for 70  $\mu$ sec prior to acquisition of data. A delayed acquisition of 70  $\mu$ sec was also used for the standard CP-MAS experiment, which ensures that the same phase correction is applied to the two sets of data.

Deconvolution by the procedure described above yields the carbon type analysis shown as below.

<u>Carbon Type</u>	<u>% Content</u>	<u>Carbon Type</u>	<u>% Content</u>
Aliphatic Me	6	Aromatic CH	5
Chain C <sub>2</sub>	4	Aromatic quaternary	11
Main chain -CH <sub>2</sub> -	41	Aromatic CO	3
Aliphatic CH	12	-CH <sub>2</sub> O-	7
Aliphatic quaternary	2	-CHO-	3
Aromatic Me	3	-CO <sub>2</sub> R	1
		-CO-	1

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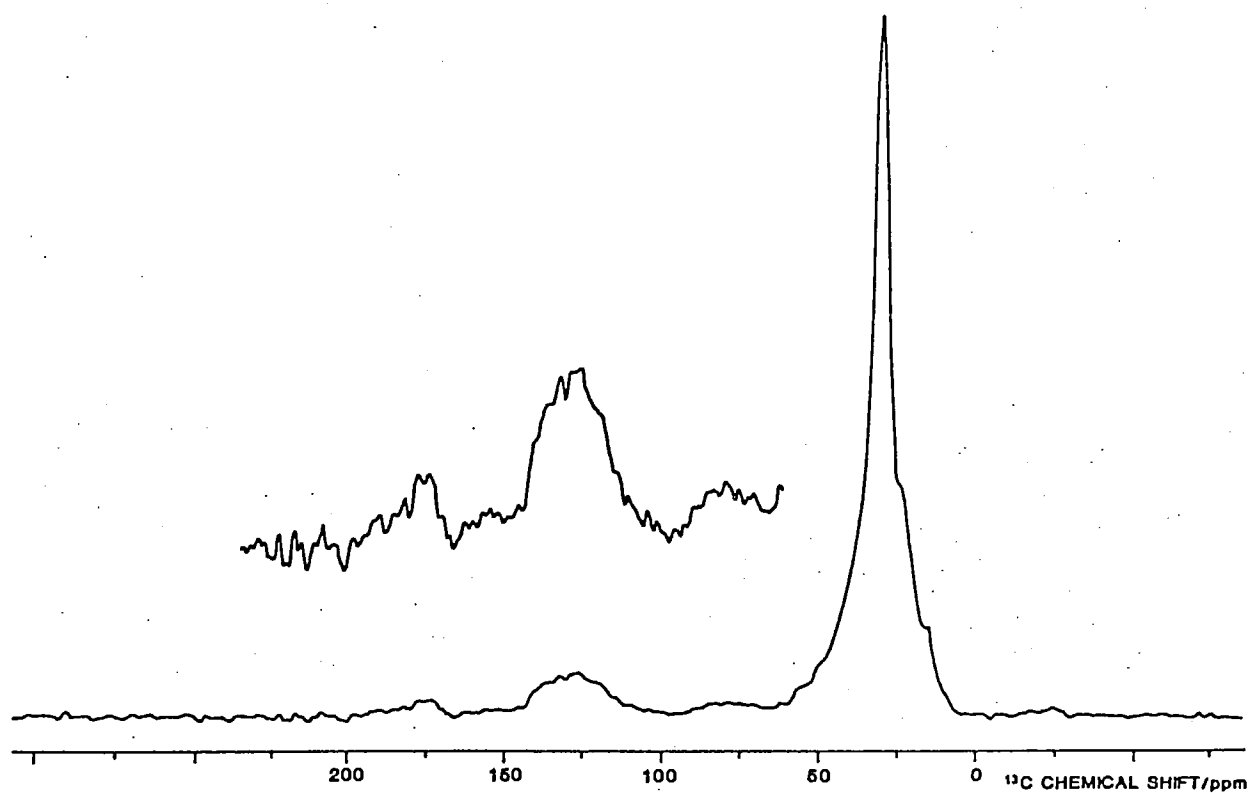


FIG 1  $^{13}\text{C}$  CP/MAS NMR SPECTRUM OF GREEN RIVER OIL SHALE KEROGEN

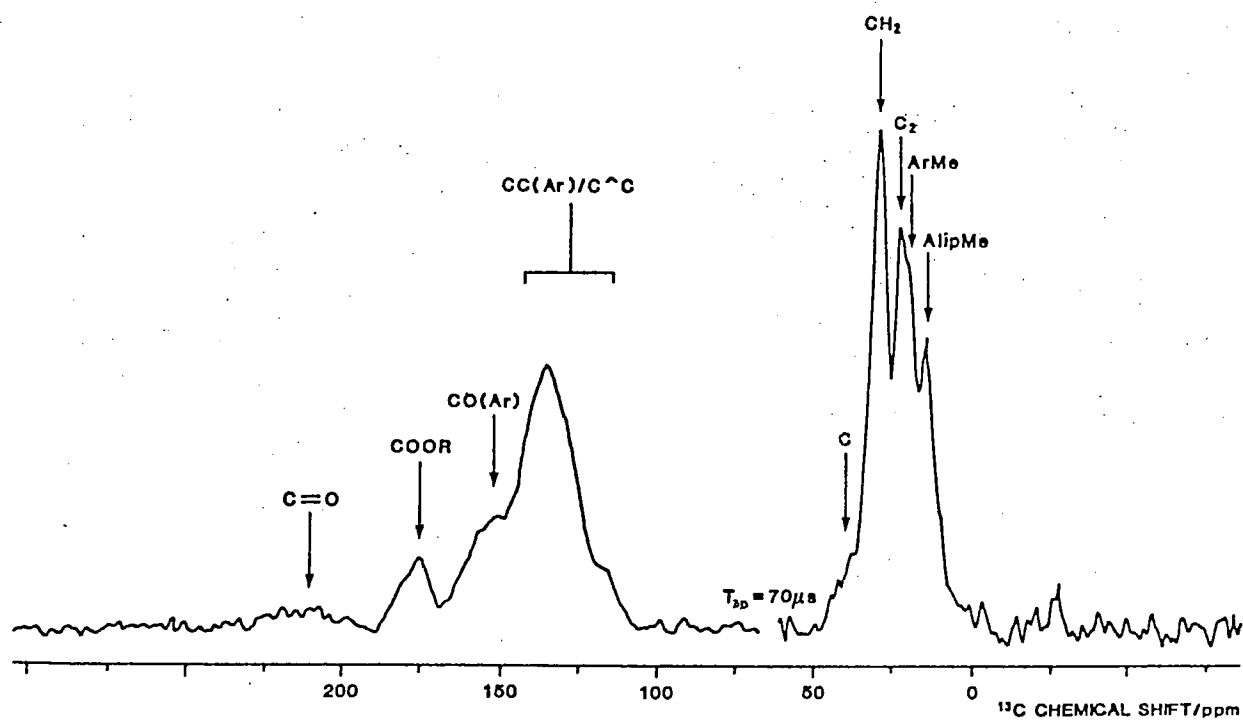
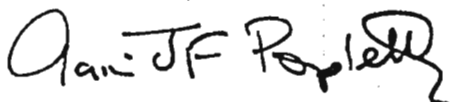


FIG 2 ASSIGNMENTS OF CARBON RESONANCES IN DIPOLAR DEPHASED SPECTRA

From this data a mass balance of  $C_{100}H_{152}O_7$  is calculated, which compares very well with the elemental analysis,  $C_{100}H_{159}N_{2.9}O_{5.5}S_{0.8}$ .

Yours sincerely



DR I J F POPLETT  
Spectroscopy Branch



National Research Council  
Canada

Division of Chemistry

Ottawa, Canada  
K1A 0R6

Conseil national de recherches  
Canada

Division de chimie

24 March 1986

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

Dear Barry,

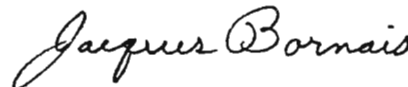
Re: Data Transfer between an ASPECT-3000 and a VAX 11/780

Some programs have been reported for transferring data files between Bruker NMR spectrometers and a VAX (TAMU NMR #317-29 and #328-18). Our requirements are that the typewriter of the spectrometer console act as a terminal for the VAX in a timesharing mode with the normal NMR operations and that there be only one RS232 line between the ASPECT 3000 and the VAX. The ASPECT end of the operations are controlled by a program VAXCOM while the VAX is run with a slightly modified version of VAXNET (TAMU NMR #317). We can transfer data files at 9600 baud while acquiring and processing NMR spectra, all from the NMR console. The program VAXCOM and some ancillary programs will be submitted to ABACUS, the Bruker users group, in the near future.

Yours truly,

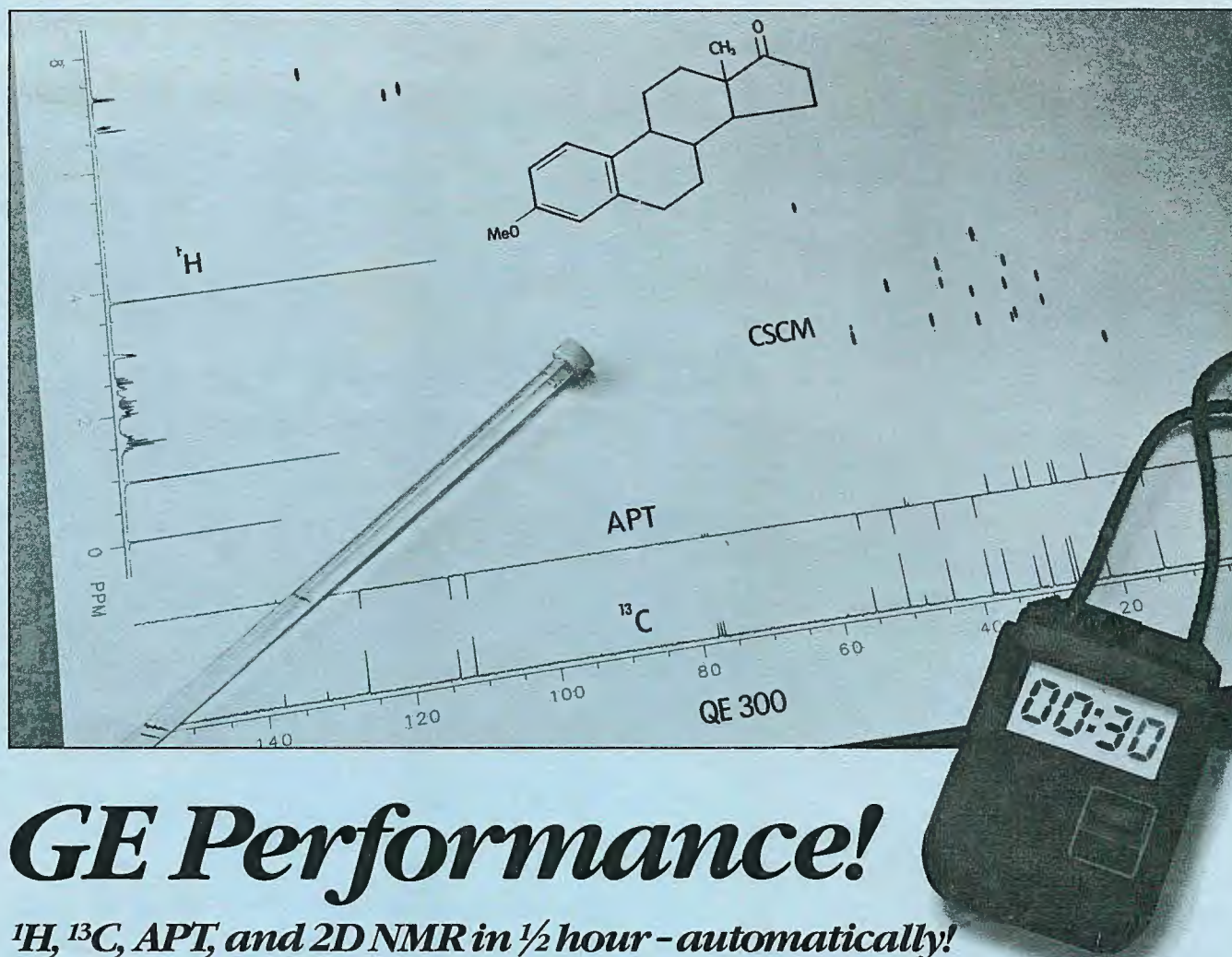


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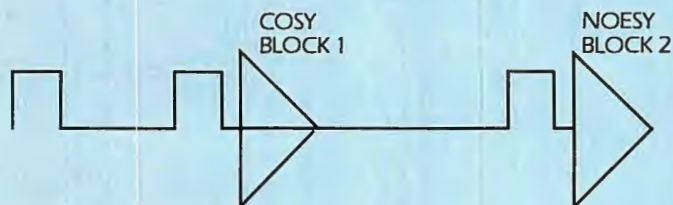
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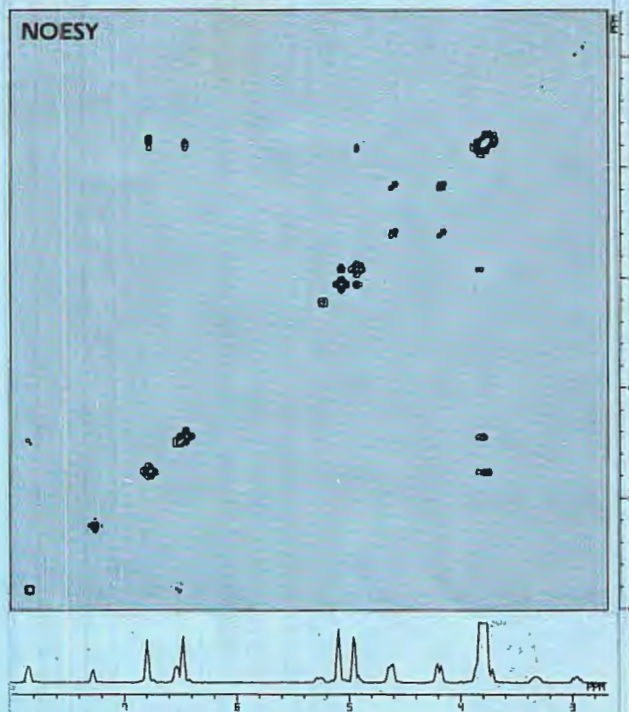
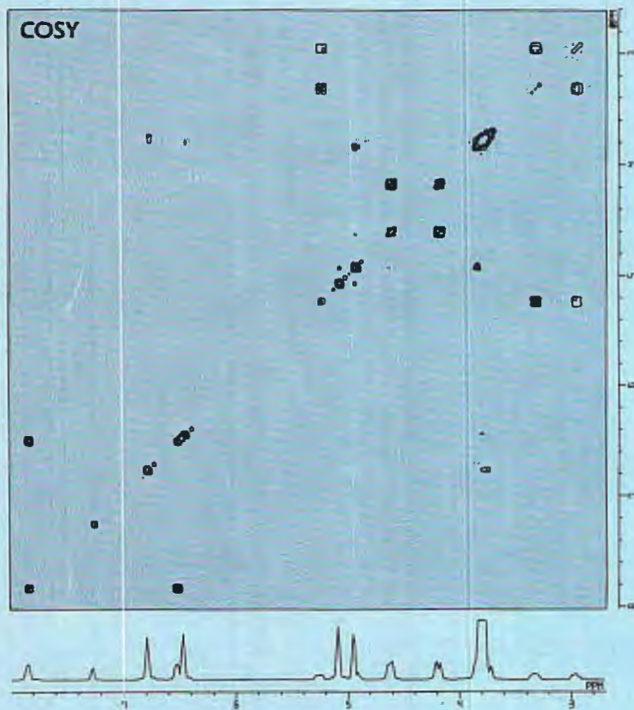
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