Brian D. Sykes

TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 344

May 1987

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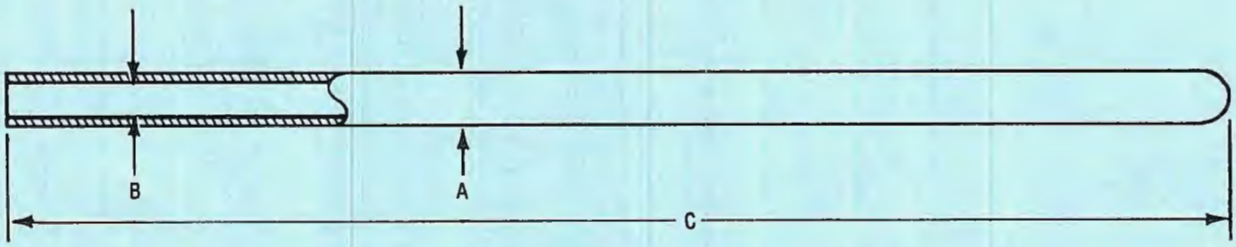

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AUTHOR INDEX -------- TAMU NMR NEWSLETTER, NO. 344, MAY 1987

ADVERTISERS

FORTHCOMING NMR MEETINGS

8th International Meeting "NMR Spectroscopy" - July 5-10, 1987; University of Kent at Canterbury, England; For information, contact Dr. John F. Gibson, Royal Society of Chemistry, Burlington House, London W1V OBN, England. See Newsletter #338, p. 55 for information and application.

29th Rocky Mountain Conference - August 2-6, 1987; Radisson Hotel, Denver, Colorado; Program Chair: Michael Reddy, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002, (303) 236-3617; Nuclear Magnetic Resonance Symposium: James Haw, Department of Chemistry, Texas A&M University, College Station, Texas 77843, (409) 845-1966; Preliminary program and pre-registration information available from Sandy Grande, 8780 W. Quarto Circle, Littleton, Colorado 80213.

In Vivo NMR Spectroscopy Summer School - August 31-September 5, 1987; University of Orleans, Orleans, France. See page 23 of this issue of the Newsletter.

26th Eastern Analytical Symposium - September 13-18, 1987; New York Hilton Hotel, New York, New York; For information, contact J.P. Luongo, AT&T Bell Laboratories, Room 1A-352, Murray Hill, New Jersey 07974, (201) 846-1582.

FACSS XIV - October 4-9, 1987; Detroit, Michigan; For information, contact Dr. Stephen J. Swarin, Publicity Chairman, Analytical Chemistry Department, General Motors Research Labs, Warren, Michigan 48090-9055, 313-986-0806.

Fritz Haber International Workshop on Modern Techniques in Magnetic Resonance - December 13-17, 1987; Weizman Institute of Science, Rehovot, Israel; See page 7 of this Newsletter for additional information.

29th ENC (Experimental NMR Conference) - April 17-21, 1988; Rochester, New York; Chairman: Professor Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, (215) 898-6459. For information, contact Dr. Charles G. Wade, ENC Secretary, IBM Instruments, Inc., 40 West Brokaw Road, San Jose, California 95110, (408) 282-3641.

Additional listings of meetings, etc., are invited.

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. 346 (July) ---------- 26 June 1987

No. 347 (August) -------- 31 July 1987

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CENTRAL RESEARCH & DEVELOPMENT DEPARTMENT
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1987 March 21

(Received 2 April 1987)

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

NMR Processing on a VAX Network

Dear Barry,

An elusive goal of many of us in the NMR community is to be able to process our data on a decent mainframe computer. This involves transferring data from various manufacturers' spectrometers to the mainframe, and having useful software there with which to process and analyze it. Here, we've been doing this in various ad-hoc ways for some years, and finally have a solution which is routine and is satisfactory for a group of users.

How can one get data to the VAX? Chemagnetics and Varian provide this capability with their spectrometers, but at this time we own primarily Bruker and GE machines. Since we have a VAX solely for spectroscopic work, we can use dedicated 9600 baud serial lines for communication with a WM-400, a CXP-300, two NT-360s, two NT-300s, a QE-300, an NT-200 and two GE data stations. To mediate file transfer, Nicolet's[1] VAXTRN program is used on the TMON and DEXTER systems, and NMRi's[2] Pascal program TF works on these and on the ADAKOS systems. A VXR-500 is also being linked via Ethernet, and VNMR files are directly Fortran-readable. We expect to add more VXRs & MSLs to this network.

After transferring data to the VAX, we'd like to make the data available to chemists at their desk-top terminals and PCs. Initially, we purchased NMR1[2], a large Fortran-77 program, for this purpose. NMR1 appeared attractive because it supports file transfer from all GE and Bruker spectrometers, supports a variety of terminals, and claimed to support DAVINS, LAOCOON, DNMR5, polymer sequencing, kinetics analysis, MEM, etc.

It does support terminals well, and its lineshape fitting is useful. It has its share of inconveniences (features?) to be avoided, such as automatic phasing, and many incomplete or unsupported features. However, we have found to date several dozen errors in this program. Some are "bugs" which produce fatal crashes of the program. More serious are those bugs which produce incorrect answers but may escape casual observation. NMRi has not been able to provide the resources to fix these problems at the rate they are discovered under only occasional use, nor even to respond to most bug reports. Many desirable parts of NMR1, such as polymer analysis, regression analysis, and process control, have proven unusable, despite some persistant attempts here.

NMR1 apparently evolved from the work of many student authors over many years, and I'm sure it is not easy to maintain or upgrade. We can only hope that anyone using NMR1 is possessed of great patience, and a critical eye for wrong answers.

VNMR[3], in its VAX form as announced by Varian at the 1986 ENC, has been used here. But we've gotten conflicting statements from Varian as to whether they will/will not sell VNMR separate from a new spectrometer, can cope with the concept of multi-processor (cluster or site)

licensing, or will/will not keep the data file format a trade secret, even from their own customers. We hope that Varian resolves these questions soon. I wonder how many spectroscopists around the world are now playing Sherlock Holmes, divining VNMR file format by trial and error?

We have at last found a practical, comprehensive and error-free NMR processing program for our VAXes. It is FTNMR[4], written by Dennis Hare. FTNMR is command (not menu) driven, so one has to make the effort of learning its commands. But users then find it easy, rational, straightforward and fast. New macro capabilities allow one to build menus, making life easier for new or occasional users. FTNMR runs at over twice the speed of NMR1 in computationally intensive tasks, such as FT, apodization, and calculation of contours. Its internal structure, based on a "stack" of spectra analogous to the stack of numbers in an Hp calculator, is powerful and flexible, making comparison of spectra (impossible in NMR1) easy. Operations such as 2D processing are extremely easy to automate as "macros", simple lists of FTNMR commands. We found it was readily interfaced with John Skilling's excellent MEM software[5], and other local routines have been readily incorporated; the source is elegant. FTNMR's primary weakness is simply a lack of documentation.

FTNMR is, in intent and design, a processing program; NMR1/NMR2 are processing and analysis programs. We can compare only the processing features, as we have not found NMR1's analysis features to be supported, or adequately documented, or usable.

I'd be interested in corresponding with others who might be converting NMR1/ NMR2, GE (VAXTRN) and VNMR files into FTNMR format. For GE, Bruker or JEOL spectrometers equipped with tape drives, FTNMR can read these tapes directly. Both microVAX and Sun workstations, which I'm sure will be in abundance at the ENC, will be moving more and more NMR data into the DECnet world... and probably will still leave it to users to resolve file format incompatibilities.

At Du Pont, key contributions to the work described above have been made by Peter Domaille, J. Mac Read, Aaron Owens, David Filkin, Fred Davidson and Ray Ferguson. Please credit this letter to D. D. Bly's account.

I hope other readers will share similar experiences here (alas, there's no Better Business Bureau for NMR software!). Any opinions stated here are mine personally, not those of my employer.

Sincerely,

Rod Farlee

Rodney D. Farlee

[1] VAXTRN or NIC-COM™, Nicolet Analytical Instruments, 5225-1 Verona Road, Madison, WI 53711.

[2] LAB-ONE™ NMR1, New Methods Research, Inc., c/o NIH Resource, Brown Hall, Syracuse University, Syracuse, NY 13210.

[3] VNMR™, Varian Associates, Palo Alto, CA.

[4] FTNMR™, Hare Research, Inc., Woodinville, WA; available through M+R Resources, P. O. Box 642, Ashburnham, MA 01430.

[5] J. K. Skilling, Maximum Entropy Data Consultants, St. John's College, Cambridge, CB2 1TP, England.

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24 March, 1987
(Received 30 March 1987)

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

Short title: Chemical shift imaging

Dear Professor Shapiro:

NMR imaging is maturing rapidly and is finding distinct applications in several fields of study. Present NMR imaging systems are being configured to image objects varying in size from 5 to 500 mm at magnetic flux densities from 0.15 T up to 9.4 T. Imaging small objects with high spatial resolution at the highest flux density presents the greatest challenge. A delicate balance must be maintained between spatial resolution and available signal-to-noise ratio to produce high quality images in a reasonable period of time. At the same time, the rich information content of NMR becomes accessible at high magnetic fields as the chemical shift effect begins to dominate the inherent magnet inhomogeneity. However, the chemical shift can distort the image so the usual solution is to overcome the chemical shift effect with increased gradient strength. This comes at the price of reduced signal-to-noise ratio in the resulting image (see TAMU NMR Newsletter 333, p.6, 1986). We have been considering ways to produce high quality images and retain the information content of the NMR spectrum. We would like to report on one approach we have taken to accomplish this goal with chemical shift imaging.

The basic idea of our technique is to create an image which is dominated by the chemical shift effect. An example is shown in the figure. The pulse sequence is a modification of the chemical shift imaging sequence reported by Sepponen et al (see JCAT 8, p.585, 1984). In the original technique, the temporal position of the refocusing pulse was stepped to define a third axis representing the spectral information. In our technique, the phase-encode gradient and temporal position of the refocusing pulse are stepped simultaneously. This reduces the three-dimensional technique to a two-dimensional technique with the information from spatial position and chemical shift convoluted along one axis. If the chemical shift dominates, the image of the object derived from each chemically shifted resonance can be cleanly separated from all others. With the particular choice parameters used to create the image in the figure, the images lie along a 45 degree diagonal.

This technique is most suitable for imaging small objects at high magnetic fields where the chemical shift dominates both the magnet inhomogeneity and spatial information. Also this technique allows one to optimize signal-to-noise ratio by reducing the gradient level to that just necessary to overcome magnet

inhomogeneity. The reduction of the three-dimensional data matrix to a two-dimensional matrix is a significant savings in experimental time and the technique can be extended to produce a volume chemical shift image in three dimensions.

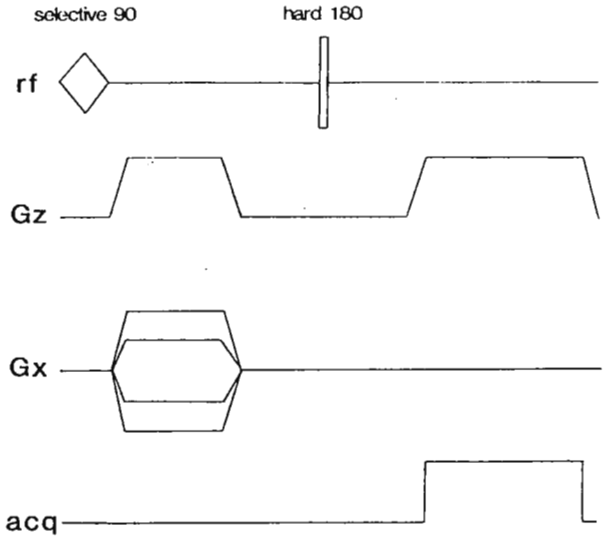
Sincerely yours,

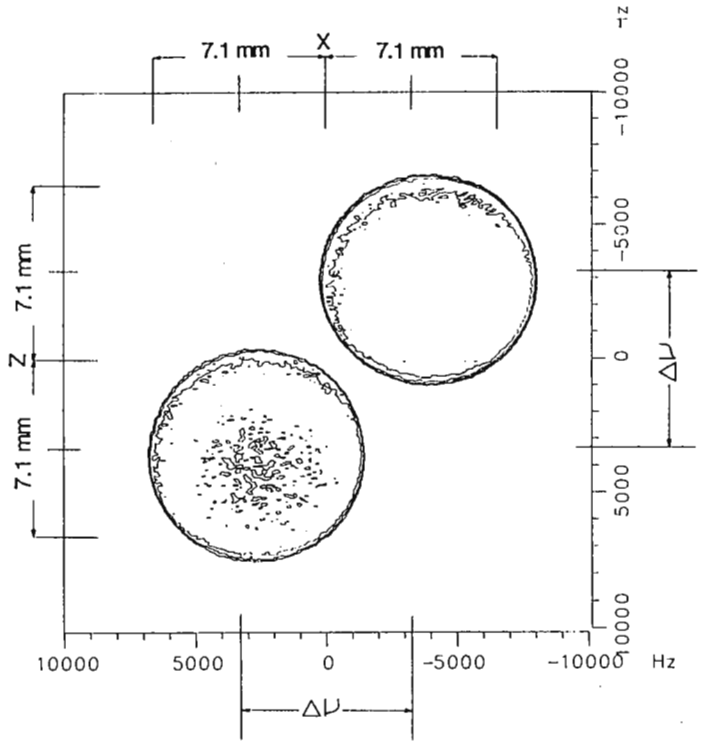
Tom Mareci Michael D. Cockman

T. H. Mareci and M. D. Cockman

BITNET: userid, @40F3U@ (Because of the @ characters in this userid, the EMAIL
node, NERVM command of BITNET will not work with this userid)

Convolution Chemical Shift Imaging





DEPARTMENT OF HEALTH & HUMAN SERVICES

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March 30, 1987 (Received 16 April 1987)

Professor Barry Shapiro
TAMU NMR Newsletter
Department of Chemistry
Texas A & M University
College Station, Texas 77843-3255

Improved Shield for In Vivo Probe; Positions Available

Dear Barry:

We have constructed an *in vivo* probe for our vertical wide bore magnet/Varian XL-400 system. The probe is conveniently designed with removeable copper brackets that have either singly or doubly tuned coils, or concentric coils, and we have observed P-31, H-1, and C-13 spectra of subcutaneous human tumors grown in nude mice in this system (1).

Initially we used a copper cradle to hold the mouse, which acted as a Faraday shield to reduce the signals from the body of the animal, in order to observe the signals from the tumor projecting through a hole in the cradle (2). However, we and others found that the copper shield causes significant line-broadening, presumably from diamagnetic and eddy effects. Using a phantom consisting of two compartments, one containing Pi and the other ATP, we quantitated both the P-31 line broadening and shielding effects, comparing the copper cradle to a plastic one. In order to optimize the arrangement we found that a piece of copper foil placed between the mouse and the plastic cradle is a good compromise, in that it does provide adequate shielding without causing significant line broadening. This is a minor modification, but gave the best *in vivo* P-31 spectra we have yet seen from tumors.

I have a position available for an Electronics Technician/Engineer to work in the new NIH NMR Center (with 2T and 4.7T CSI animal systems and a whole body 1.5T GE-Signa machine). I would also be interested in a post-doctoral fellow (US or foreign citizen) with experience in 2D-NMR for oligonucleotide work.

Sincerely,

Robbe C. Lyon

Jack S. Cohen

1. R. Lyon, R.G. Tschudin & J.S. Cohen, *Proc. Soc. Mag. Res. Med*, Montreal, 1986, p. 217, and paper in preparation.
2. T.C. Ng, W.T. Evanochko, & J.D. Glickson, *J. Mag. Res.* 49 526, 1982.

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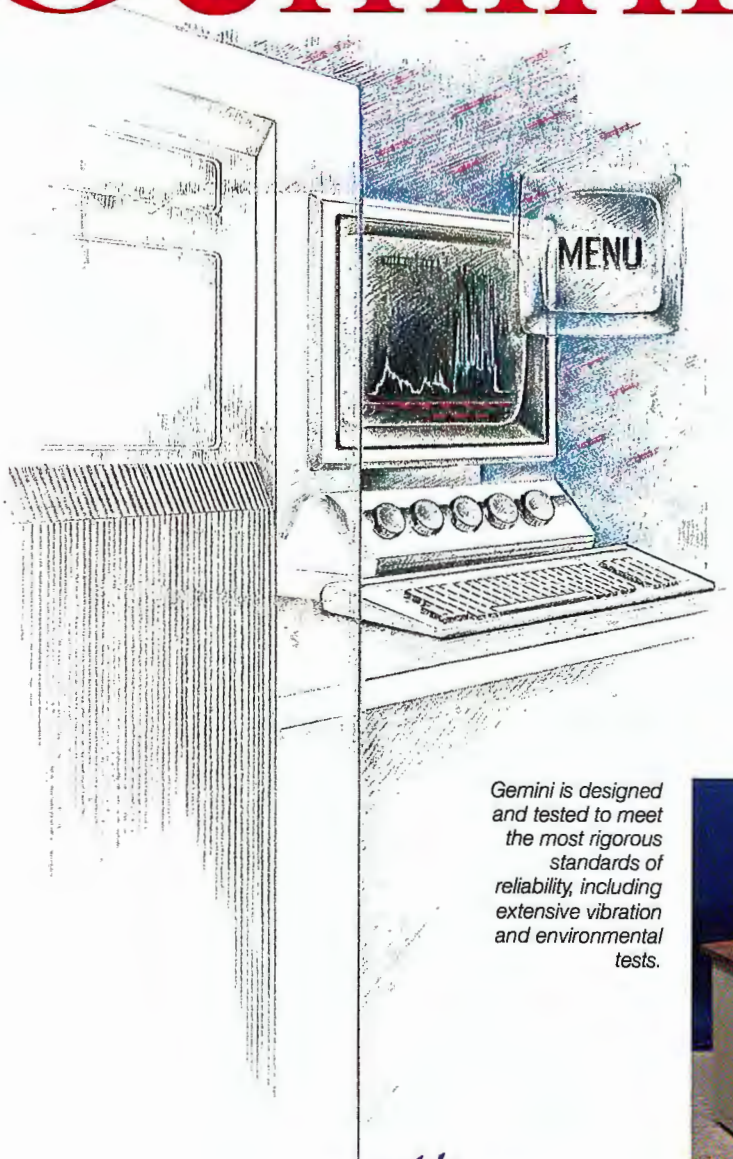

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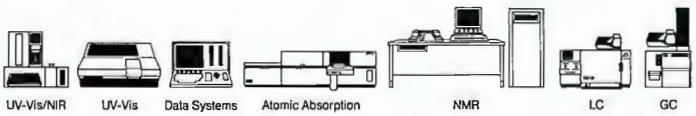

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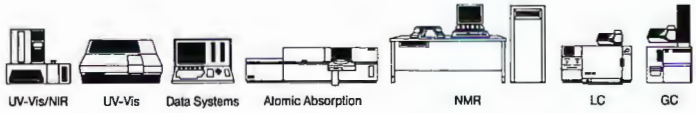

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DEPARTMENT OF CHEMISTRY

(Received 24 April 1987)

PROTON-FLUORINE COUPLING IN RIGID RING SUGARS

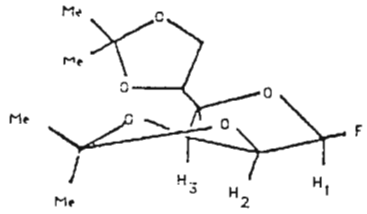
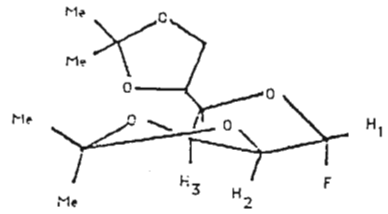
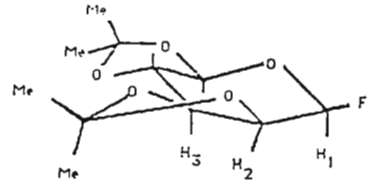
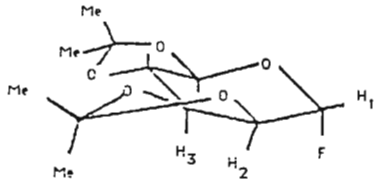
M.J. Minch, Yong Ma, Paul Gross, and Ken Drew

Sir:

Vicinal proton coupling constants are a function of the electronegativity of all substituents bound to the H-C-C-H fragment and the time averaged orientation of each substituent with respect to the coupled proton pair. The effect of the electronegativity of a variety of substituents is most clearly revealed in rigid ring systems where orientations are well defined. A number of semi-empirical Karplus-type equations, corrected for substituent electronegativity, have been developed from J-values for rigid ring proton couplings. This includes the equation of Altona and coworkers[1] which is based on 315 experimental coupling constants, for a wide range of rigid compounds and substituents.

Because of our special interest in carbohydrate conformational analysis and because the Altona dataset (unpublished) is heavily weighted by oxygen and halogen substituents, we have undertaken a 360 MHz ^1H study of amino substituted benzyl 4,6-O-benzylidene β-D-allo, α-D-altro, α-D-gluco and α-D-mannopyranosides as well as the isomeric benzyl 4,6-O-benzylidene β-D-manno and α-D-allo 2,3-oxiranes. The 4,6-O-benzylidene and 2,3-oxirane ring fusions impose considerable conformational constraint on the pyranoside ring. The former holds the pyranoside ring in a rigid $^4C_1$ conformation while the latter forces a 90° dihedral angle between H_3 and H_4. A complete analysis of all nonaromatic proton resonances has afforded 56 ^3J-values for a wide range of substituents including nitrogen and sulfur. The torsion angles of a representative compound have been determined by x-ray crystallography.

For the same reason we have determined the vicinal proton-proton and proton-fluorine coupling constants for the isomeric 2,3:5,6-di-O-isopropylideno α-D-manno and β-D-manno furanosyl fluorides and 2,3:4,6-di-O-isopropylideno α-D-manno and β-D-mannopyranosyl fluorides. It is these latter data that we wish to report here.

Compound		$^2J_{H_1F}$	$^3J_{H_2F}$	$^3J_{H_1H_2}$
		(Hz)	(Hz)	(Hz)
α-D-manno furanosyl		59.2	6.3	<0.2
β-D-manno furanosyl		66.7	15.4	3.6
α-D-manno pyranosyl		49.3	6.5	<0.2
β-D-manno pyranosyl		60.1	28	2.15

The geminal HF coupling constants are within the range observed for an F bonded to an sp^3 hybridized C but the values we observed are well above the average established primarily from conformationally mobile compounds.[2,3] The variation in $^2J_{H\ F}$ (17.8 Hz) is surprisingly large considering that the β-substituents are the same in all four cases. This points out the importance of β-substituent orientation on HF geminal coupling.

Respectfully,

Mike

Michael J. Minch Yong Ma Paul Gross Ken Drew

1. C.A.G. Haasnoot, F.A.A.M. DeLeeuw, and C. Altona, Tetrahedron, 36, 2783-2792 (1980).

2. V. Wray, in Ann. Report NMR Spectroscopy, G.A. Webb, ed., Vol. 14 (1983).

3. L.D. Hall, J.F. Manville and N.S. Bhacca, Canad. J. Chem., 47, 1-17 (1969).

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service

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April 15, 1987

(Received 24 April 1987)

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

Fluorine-19 NMR Studies of Methoxyflurane Metabolite Excretions

Dear Dr. Shapiro,

I would like to begin a subscription to the TAMU NMR Newsletter. I have been told that the subscription fee is a contribution to the Newsletter. If other payment is necessary, i.e. money, NMR time, turnip blood, please let me know. Please send the subscription and any other correspondence to the address listed below.

One of the areas of interest of our group at the National Institute of Environmental Health Sciences is the metabolism of inhalation anesthetics, specifically the fluorinated anesthetics halothane and methoxyflurane (MOF). MOF (2,2-dichloro-1,1-difluoro-1-methoxyethane) has been proposed to be metabolized to 2,2-difluoro-2-methoxyacetate, inorganic fluoride, dichloroacetate, and oxalate. However, previous methods used to identify and quantitate 2,2-difluoro-2-methoxyacetate are tedious and subject to error. Therefore, we decided to use fluorine-19 NMR to try to quantitate this metabolite.

Shown in Figure 1 is a fluorine-19 NMR spectrum of urine collected from a Sprague-Dawley rat 7 hours after a one hour administration of MOF. The spectrum has two resonances, identified as 2,2-difluoro-2-methoxyacetate and fluoride by "spiking" the urine with authentic compounds. We have collected rat urine as a function of time following MOF administration (always a fun task) and have quantitated both fluorine-containing MOF metabolites using standard curves of MOF metabolites in urine collected from control animals. The time course of clearance of the two MOF metabolites is shown in Figure 2. We have checked the fluoride concentrations calculated by NMR using a fluoride ion-selective electrode, and find that the two methods agree within 20%.

Future experiments include trying to measure concentrations of dichloroacetate in rat urine by water-suppressed proton NMR.

Sincerely,

Barry S. Selinsky
NIEHS
Box 12233 MD 5-01
Research Triangle Park, NC 27709

FIGURE 1. ^{19}F NMR spectrum of 0.5 ml of rat urine collected 7 hours after a one hour exposure to methoxyflurane. Chemical shifts are referenced to external trifluoroacetic acid.

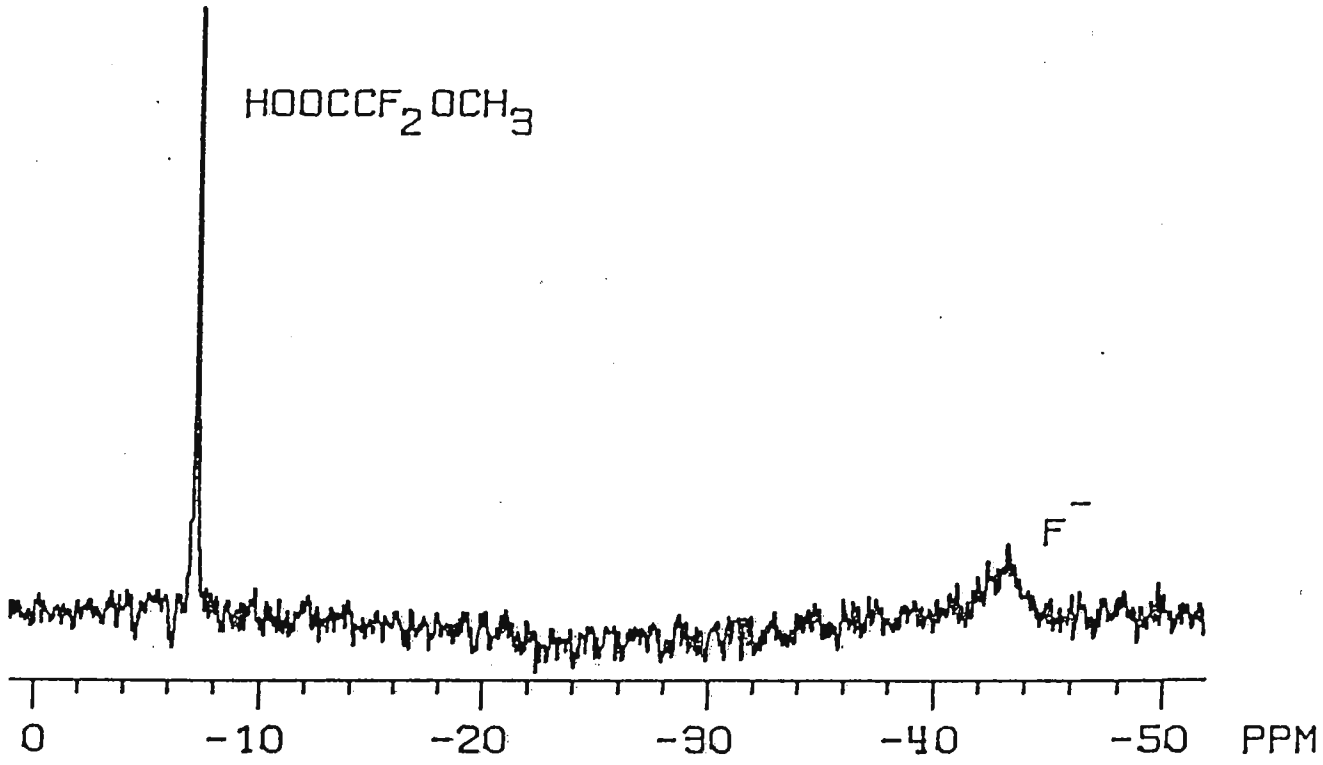
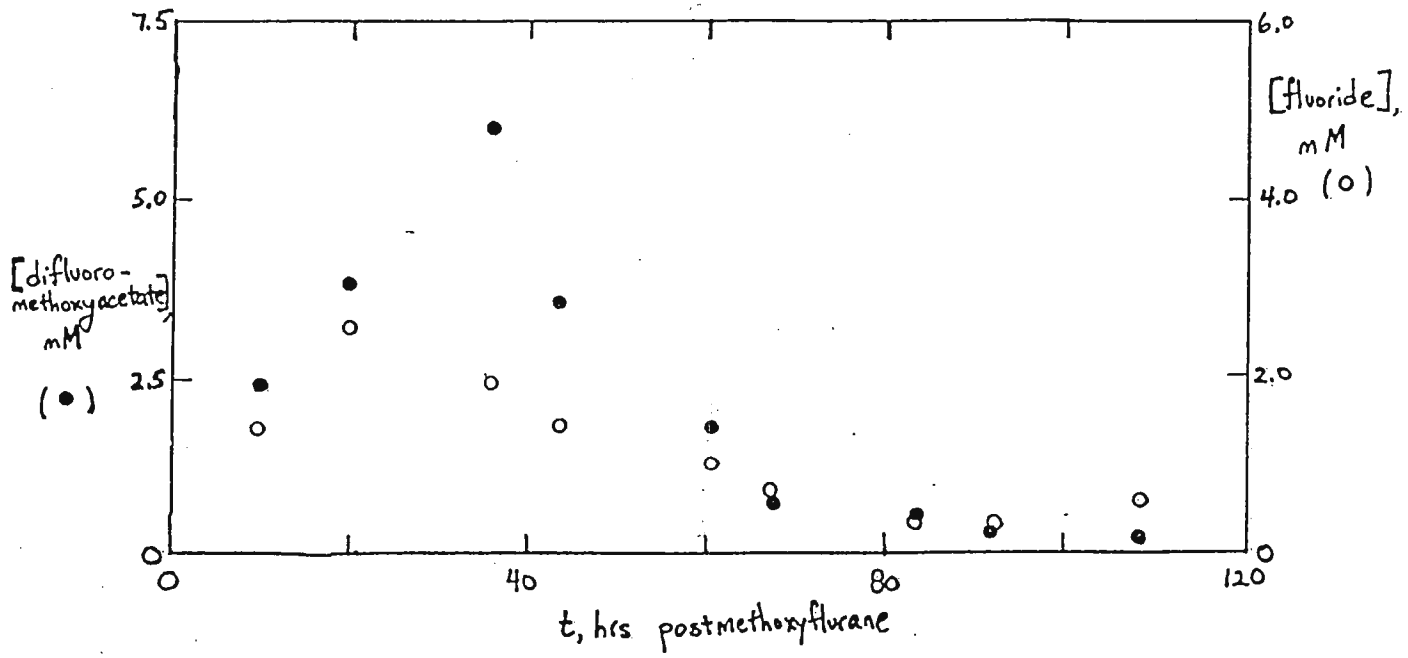


FIGURE 2. Time course of excretion of methoxyflurane metabolites from the rat after a one hour exposure to MOF. Data shown are collected from one rat.



THE UNIVERSITY OF MANITOBA DEPARTMENT OF CHEMISTRY Winnipeg, Manitoba
Canada R3T 2N2

March 24, 1987. (Received 30 March 1987)

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

Title: ASPECT 3000 DMA Interference. HP7550A Graphics Software

Dear Prof. Shapiro:

We have recently solved -- I think -- an annoying problem with the ASPECT 3000 computer on our AM300 spectrometer. The problem would occur during concurrent acquisition and processing and would result in the swapping, in midscan, of the channels A and B of the acquired data, equivalent to a 90° receiver phase shift.

At first we suspected the bit in the digitizer control word which selects the sampling order, but lengthy monitoring proved that this was not the case. Because the problem seemed related to FT processor activity we then concluded that FT processor DMA activity was interfering with the DMA address generator on the digitizer board (how or why we haven't a clue!). Because Bruker uses sequential sampling this could have the same effect as swapping the channels. Our solution, which was rather BFI*, was to re-order the boards in the computer so that the FT processor is between the memory board and the digitizer board. Care must be taken, however, because the computer's internal cabling restricts the board order somewhat. After much trial and error we arrived at the following board sequence: CPU, memory, IO, Disk, FT processor, digitizer, pulse programmer, floppy, blank, blank, bus controller, filter/PLL. I don't know whether this problem is common, but anyone experiencing spurious channel swaps may want to try our solution before trying expensive board replacements.

We are also developing a collection of ASPECT 3000 PASCAL procedures for driving our HP7550A plotter, suitable for annotating spectra, drawing diagrams or whatever. When finished, we intend to submit the package to ABACUS, but until then interested readers can obtain a copy from me directly.

Please credit this letter to Ted Schaefer's account.

Sincerely,

Kirk Marat,
Dept. of Chemistry.

KM:dmh

*Brute-Force and Ignorance.

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DEPARTMENT OF CHEMISTRY RIVERSIDE, CALIFORNIA 92521-0403

March 25, 1987
(Received 30 March 1987)

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

^{2}H Decoupling of Fluorine Compounds

Dear Professor Shapiro:

Recently, we have home-built a ^{2}H decoupler for Professor Morton's group in my department to study deuterated fluorine compounds or mixtures. As shown by the results on the enclosed page, it performs satisfactorily.

The principle is to mix 10 MHz with 36 MHz, filter the output 46 MHz and 2-stage amplify it to the desirable power level. We have bought a frequency mixer (ZAD-3, mini-circuits), two bandpass filters (DP, HP, Lark Engineering) and a power amplifier (400 AP ENI) as well as modifying the buffer amplifier in our original spin decoupler (NT300) for the appropriate frequency. The total cost is about $1200.

The only surprise came when we interfaced the homebuilt decoupler to a ^{19}F probe and using the lock channel for decoupling. When operated with heterodecoupling mode the S/N decreases more than 10 times (Figure 1b). It puzzled us for a while; but after we realized the observe coil is doubly tuned to ^{2}H and ^{19}F we came up with the solution, i.e., to use homodecoupling mode to remove the noises generated by the ^{2}H decoupler. And as expected, the original S/N ratio is restored (Figure 1c).

In the future, we would like to build decouplers for other nuclei such as ^{31}P.

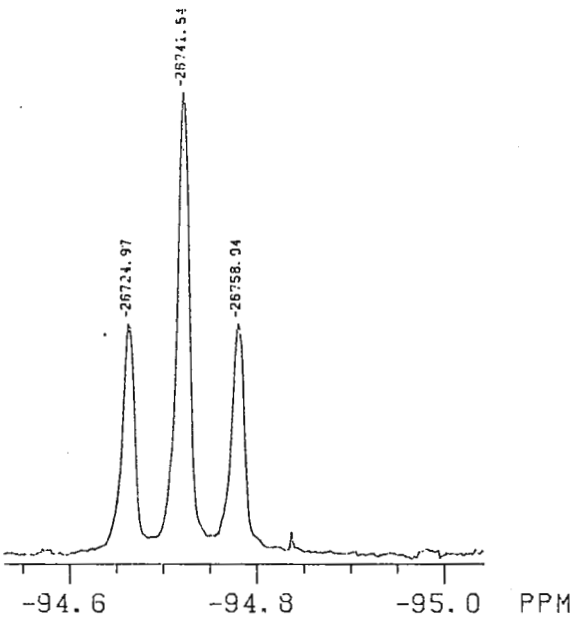
Sincerely,

Robert W.K. Lee Tom Shaler Thomas Hellman Morton

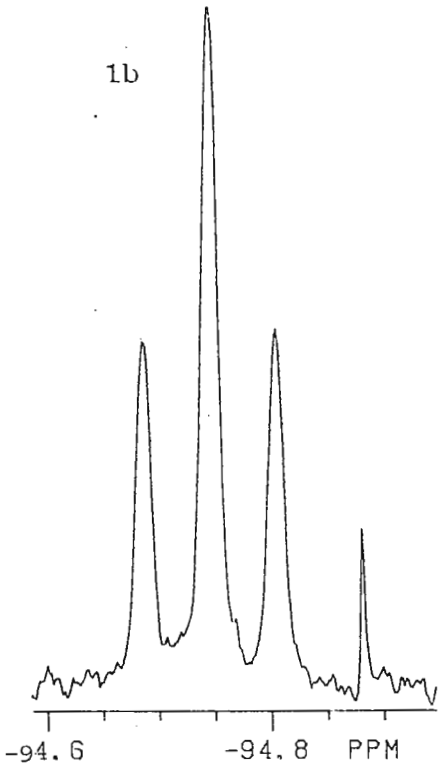
RL/nc

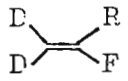
Enclosure

Figure 1c



1b



The spectra of 

R = $-(CH_2)_5CH_3$

1a

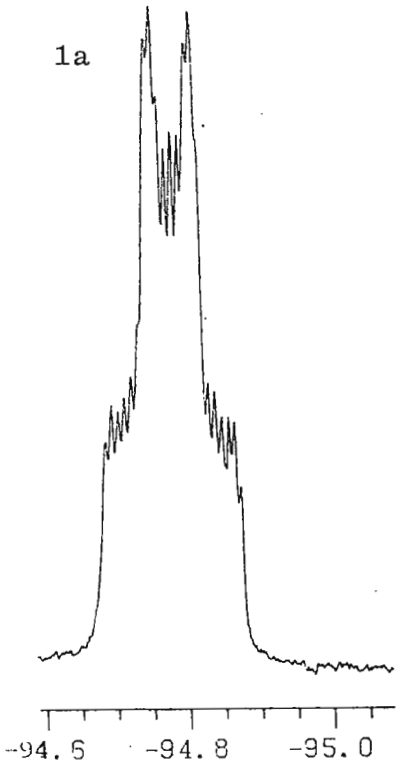


Figure 1a. 1 PULS experiment 4 scans.

1b. 1 PULS, ^2H decoupling heterodecoupling mode 64 scans.

1c. 1 PULS, ^2H decoupling homodecoupling mode 4 scans.

Shell Development Company
A Division of Shell Oil Company

Westhollow Research Center
P. O. Box 1380
Houston, Texas 77001

March 26, 1987 (Received 16 April 1987)

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

Dear Professor Shapiro,

SUBJECT: SOLID STATE NMR OF TIN COMPOUNDS

Although Magic angle spinning (MAS), high power decoupling and cross polarization (CP) techniques in solid state NMR (SSNMR) have been in use for several years, the reported applications have largely been limited to carbon (^{13}C) and to a smaller extent to silicon (^{29}Si) and phosphorus (^{31}P). However, the potential of these techniques in elucidating the structural details of organometallic solids is very high and can also be be used for nuclei such as tin (^{119}Sn, 8.6%), mercury (^{199}Hg, 16.8%) and lead (^{207}Pb, 22.6%). All three are spin 1/2 nuclei and of significantly higher abundance than carbon. Part of the reason for paucity of open literature reports of NMR in solid state of these nuclei stems from technical difficulties. In particular, tin is well known for the large spread in its shielding anisotropy. Till today, there have been few reports of solid state NMR applied to tin compounds [1-3] and all of them stress the complexities involved in understanding the spectra containing numerous spinning side bands. However, it has also been demonstrated that the chemical shift tensor characteristics can be better evaluated in a system containing such large number of side bands [2]. For NMR measurements, ^{119}Sn is roughly four times more sensitive than ^{13}C.

There is a necessity of a reliable standard to optimize the proton-tin cross polarization conditions as the tin nuclei seem to have excessively long relaxation times, similar to silicon ^{29}Si, to be observed directly. We have examined several different tin compounds for a good CP standard. Of these, tin(IV) acetate seems to be the best candidate for a standard not only to optimize the CP parameters but also to set the magic angle accurately as its free induction decay is richly decorated by the echoes resulting from spinning side bands. The shielding anisotropy in this tin compound is much smaller than in trimethyl tin fluoride [2]. It was easy to obtain the Hartmann-Hahn match required for optimum CP within eight scans using tin(IV) acetate. These conditions can then be used for any unknown tin compound of interest as a starting point.

The CP spectrum obtained with our Bruker CXP-200 (^{119}Sn at 74.06 MHz) system is shown in figure 1 (MAS at 4 KHz, recycle 5s and contact time 2ms with a H_1 of 45 KHz; referenced to liquid tetramethyl Tin at 0.0ppm).

A closer examination of the spectrum (fig.1c) indicates there are at least two inequivalent tin nuclei in this compound. An earlier crystal structure report [4] suggests there are four inequivalent tin centers in

each asymmetric unit cell. It is possible that the differences might be too subtle to resolve the four species completely with the resolution achieved under the present conditions.

Please credit this contribution to the account of Dr. L. L. Sterna.

Sincerely,

M. Narayana
Research Chemist
Analytical Department

MN/bb

References:

1. E. T. Lippmaa, M. A. Alla, T. J. Pehk and G. Engelhardt
J.Amer.Chem.Soc. 100, 1929 (1978).
2. R. K. Harris, K. J. Packer and P. Reams
Chem.Phys.Lett. 115, 16 (1985).
3. R. K. Harris, T. N. Mitchell and G. J. Nesbitt
Magn.Reson.Chem. 23, 1080 (1985).
4. N. W. Alcock and V. L. Tracy
Acta Cryst. B35, 80 (1979).

Figure Caption:

Solid state NMR spectrum of ^{119}Sn in tin (IV) acetate, obtained with cross polarization, high power decoupling and magic angle spinning; a) free induction decay, b)Fourier transformed spectrum with spectral width of 20 KHz and c) expansion of the main resonance showing the presence of inequivalent tin sites; peaks marked `ssb' are spinning side bands.

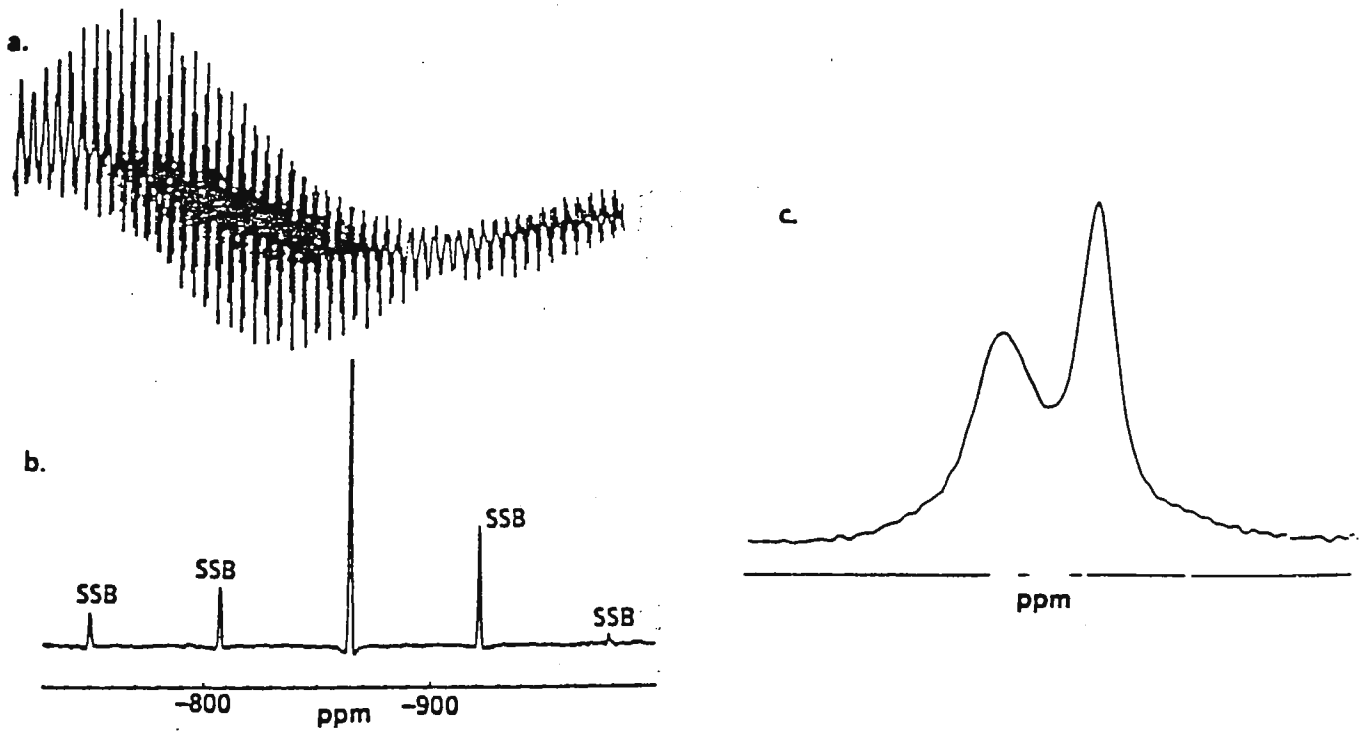


Figure 1. Solid State NMR Spectrum of ^{119}Sn in Tin (IV) Acetate, Obtained with Cross Polarization, High Power Decoupling and Magic Angle Spinning; a) Free Induction Decay, b) Fourier Transformed Spectrum with Spectral Width of 20 KHz and c) Expansion of the Main Resonance Showing the Presence of Inequivalent Tin Sites; Peaks Marked 'SSB' are Spinning Side Bands

---

Postdoctoral NMR position available at August 1, 1987 or later

Dear Dr. Shapiro

In our NMR group at the University of Berne a postdoctoral research associate position is available for an applicant with Ph.D. in chemistry, with extensive experience in magnetic resonance, particularly modern pulse techniques and a strong interest in chemical structure problems. The candidate should be cooperative and experienced in computational analysis as well as in interpretation of NMR data.
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Interested applicants should submit two letters of reference, a summary of their thesis, a list of publications and a curriculum vitae.

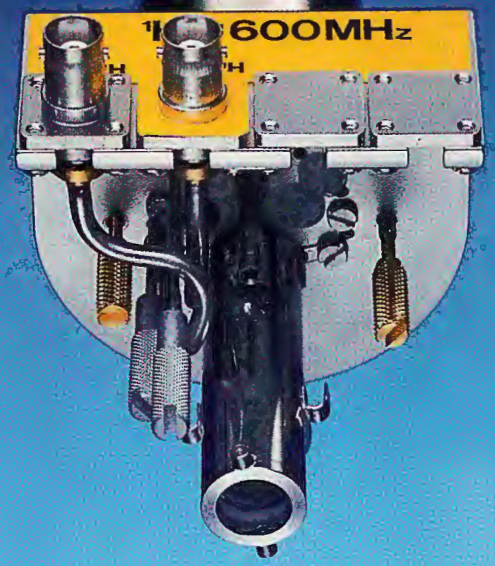
Sincerely yours

Peter Bigler

Mailing address:

Dr. P. Bigler
NMR Laboratory, Institute of Organic Chemistry
University of Berne
Freiestr. 3
CH-3012 Berne, Switzerland

Bruker delivers.



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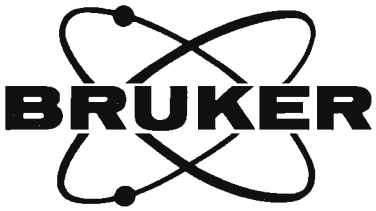

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Texas A&M University NMR Newsletter - Book Reviews

Book Review Editor - **W. B. Smith,** Texas Christian University, Fort Worth, Texas.

"Introduction to Pulse NMR Spectroscopy"

by

Thomas C. Farrar

The Farragut Press, P.O. Box 5102, Madison, Wisconsin 53605
1987; 184 pages; $14.95

Given the breadth of applications and the recent rapid development of 2D NMR, it is reasonable to expect a flood of new textbooks on the subject. Some of these are general surveys of multinuclear NMR. Others concentrate on proton or carbon NMR with a view of establishing organic molecular structures. This useful little volume by Farrar falls in yet a third area; namely, it is a lucid description of the physics of spins systems at a level which seniors or first year graduate students can comprehend. (This is my conclusion, for the author has provided no prefatory remarks indicating his intended readership.) There is no attempt at getting into spectral analysis or structure-NMR parameter relations. Given the reasonable price for what is delivered, this text would make a worthwhile introduction to one of the others which deals more with spectral interpretation. Clearly, this work is intended as an update of, and successor to, the classic introductory text by Farrar and Becker.

Following a brief introduction to the fundamental concepts of nuclear magnetic resonance, the author takes up the basic pulse experiments. A short description of modern instrumentation is inserted before returning to a more detailed account of relaxation processes. I found this chapter particularly enlightening. Indeed, throughout, there is the felicitous insertion of historical perspective which makes the reading easy.

Chapter Four deals with Fourier transform NMR calculations. The penultimate chapter introduces sensitivity enhancement techniques with a view towards the finale on 2D NMR. The latter introduces J-resolved 2D along with homonuclear and heteronuclear correlation spectroscopies.

The volume concludes with a too brief appendix on vectors and seventy-six (Why do I want to write trombones here?) key references to the literature, as well as a rather skeletal index. It is expected that a more extensive indexing will grace a second edition/printing, which is targeted for the end of 1987. This follow-up version will be typeset, rather than the serviceable but unelegantly photo-offset reproduction of the typsecript which is the present, first version. Professor Farrar has indicated privately that he would welcome receiving comments and suggestions.

W.B.S.

School of Science
Department of Chemistry

Rensselaer Polytechnic Institute Troy, New York 12180-3590

March 25, 1987 (Received 30 March 1987)

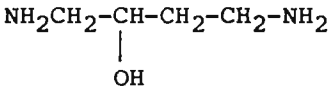
Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Title; 2-hydroxy putrescine

Dear Professor Shapiro:

In collaboration with Professors S. Bunce and D. Aikens here at R.P.I. and F. Onasch at SUNY at Delhi, NMR investigations of the protonation behavior of polyamines[1,2] have been continued with the compound 2-hydroxy putrescine.

A B C D



The proton assignments of the rather complex 200 MHz ^1H spectrum shown in Figure 1 (0.01 M in 90/10 H_2O/D_2O pH = 5.1) were established by ^1H decoupling in both H_2O and $CDCl_3$ solutions. Water preirradiation and decoupling were accomplished within the same pulse sequence by using the SETDLP (variable decoupler low power) programming element[3] on our XL-200.

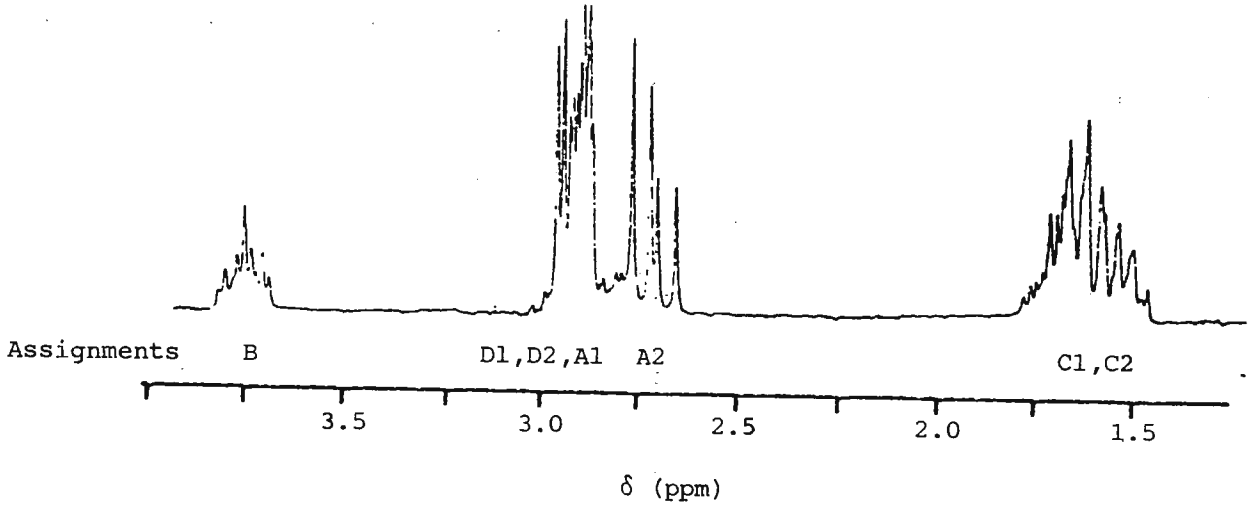


Figure 1

Simulation of the coupling patterns indicates that the protons of all three methylenes are inequivalent. However, the downfield position of methylene **D**, relative to **A** (observed at both high and low pH) is quite puzzling.

As a final check on our assigments a 2D proton-carbon correlation experiment was performed (Fig. 2).

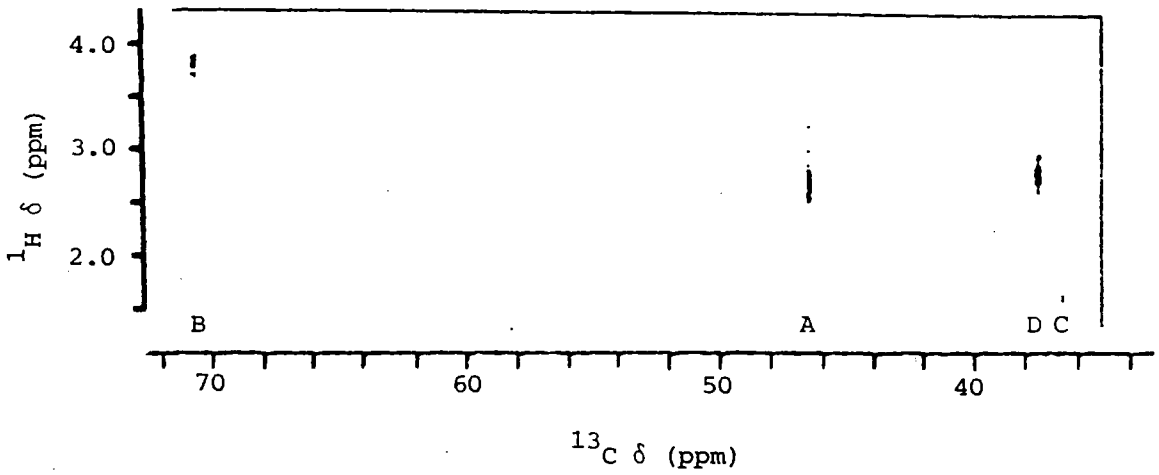


Figure 2

These results further amplify the anomalous behavior of the methylene D protons. It probably is some kind of conformational effect, but we cannot put our finger on an analogous example from the literature. We are open to suggestions on this chemical shift effect while we continue our studies of the protonation behavior.

1. D. Aikens, S. Bunce, F. Onasch, H. Schwartz, and C. Hurwitz, **J. Chem. Soc., Chem. Commun.** (1983) 43.
2. F. Onasch, D. Aikens, S. Bunce, H. Schwartz, D. Nairn, and C. Hurwitz, **Biophys. Chem.** 19 (1984) 245.
3. Magnetic Moments, I, No. 3 (1985), Varian Associates, pg. 2.

Sincerely,

Dr. Herbert M. Schwartz
Director
Major Instrumentation Center

HMS:ceg

UNIVERSITÉ RENÉ DESCARTES (PARIS V)
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DIRECTEUR : PR BERNARD P. ROQUES

Paris, March 25th 1987. (Received 8 April 1987)

Professor B.L. SHAPIRO
Department of Chemistry
Texas A & M University
College Station
TEXAS 77843-3255.

SEPARATION OF CHEMICAL EXCHANGE AND CROSS RELAXATION EFFECTS IN A DRUG NUCLEOTIDE COMPLEX

Dear Doctor Shapiro,

Still on the process in understanding the bisintercalating mode of ditercalium (1) and analogues we had to face the problem of distinguishing cross peaks coming from NOE and those from chemical exchange. One possible way to overcome this problem is to change the temperature in order to increase the exchange process and decrease the NOE effect. Unfortunately in the case of complexe between ditercalinium and oligonucleotide the possible temperature range is very limited as at low temperature the signals broadened and above 35°C the complexes precipitate.

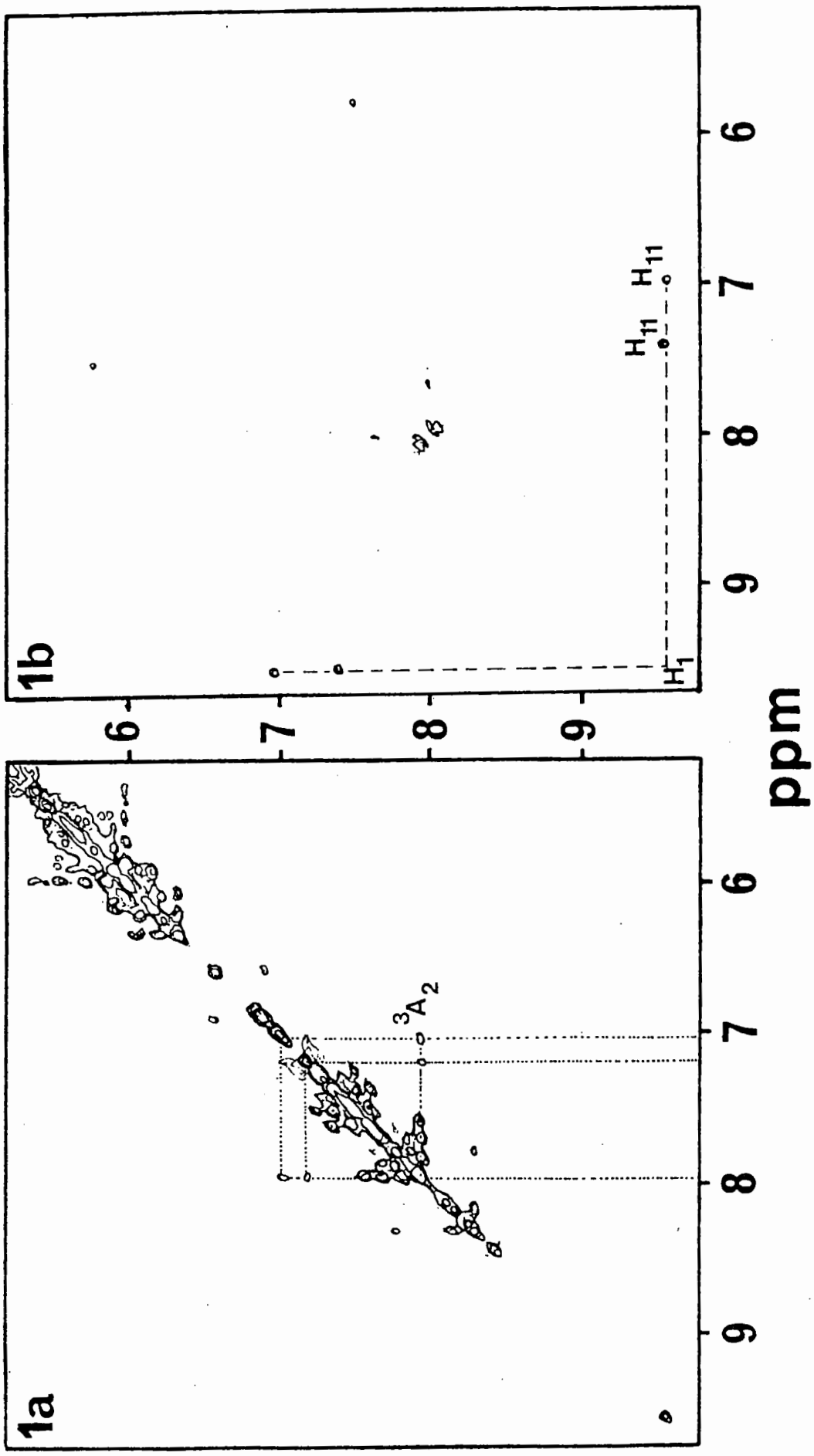
Therefore we used the 2D spin locked NOE experiment described by DAVIS and BAX (2) and based on the phase sensitive presentation in which cross peaks due to NOE have opposite phase relative to the diagonal peaks whereas the chemical exchange cross peaks are in phase with the diagonal peaks. The modification on our AM 400 MH_z Brucker spectrometer was to divid the signal issue from the PTS 160 synthetizer with a power splitter (PSC2, Mini Circuit). One part of the signal was therefore used to generate the O_1 frequency while the other part monitored the decoupler.

Figure (1) shows a 2D contour plot of first attempt of the spin locked NOE spectrum of the aromatic region of the $d(CGATCG)_2$ ditercalium complexe. The experiment was recorded at 25°C with a spin lock time of 100 msec. In 1a is represented a contour plot of resonances that are in phase with diagonal peaks. Exchange peaks for Adenine proton H_2 ($3A_2$) are indicated on the spectrum. In 1b a negative contour plot is shown and only spin locked NOE appear. In these experimental conditions only NOE corresponding to very short distances (<2Å) are observed. This is the case for H_1 and H_{11} protons of the drug.(1)

(1) A. DELBARRE, M. DELEPIERRE, C. GARBAY, J.IGOLEN, J.B. LE PECQ, B.P. ROQUES. 1987. PNAS sous presse.
(2) D.G. DAVIS, A.BAX. (1985) J.Mag. Res. 64 533-535.

J. BELLENEY. M. DELEPIERRE.

Please, credit this contribution to the subscription of Professor B.P. ROQUES.


1a
1b
$^3A_2$
H_{11}
H_{11}
H_1
6
7
8
9
ppm

Continued Progress in ^{1}H CRAMPS; Positions Available

Department of Chemistry

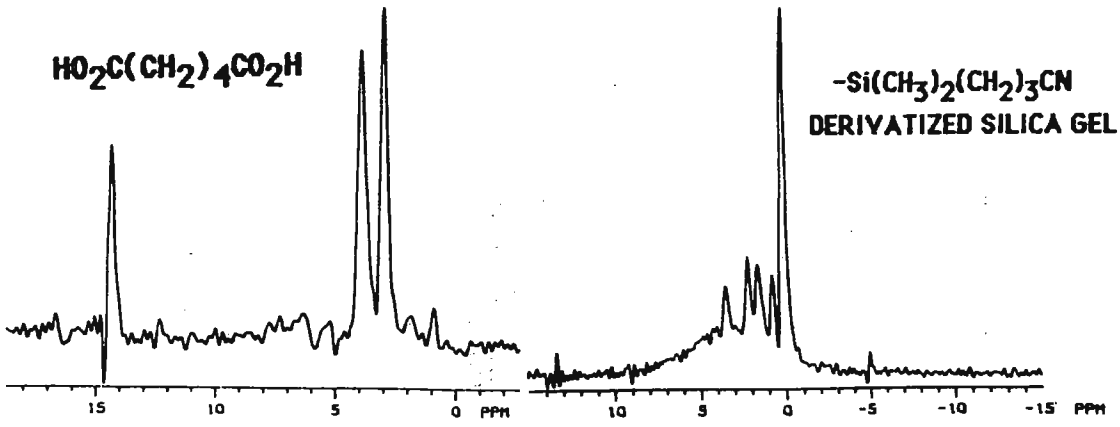
Professor B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station, TX 77843

Colorado State University
Fort Collins, Colorado
80523

April 15, 1987
(Received 20 April 1987)

Dear Barry:

Progress in the ^{1}H CRAMPS work in the Regional NMR Center continues to be excellent. Chuck Bronnimann and Bruce Hawkins are using theoretical (computer) simulations of multiple pulse phenomena as guidelines for improving ^{1}H CRAMPS performance. We encourage scientists interested in the potential of high-resolution solid-state ^{1}H NMR in their research to contact the center (303-491-6455). The two spectra below represent our current ^{1}H CRAMPS capabilities.



The Department of Chemistry has recently issued the announcement below of new positions in its Instrument Facility.

Sincerely,

Gary E. Maciel
Professor

Two Instrumentation Specialists (non tenure track) are needed in the Chemistry Department at Colorado State University. Both should be knowledgeable about Chemical Instrumentation including NMR, MS, and FTIR, familiar with the maintenance of such instrumentation, and interested in collaborative research with faculty. One will be appointed as Director of the Department Instrument Facility. This person must have a Ph.D., or equivalent professional experience, with demonstrated achievement over a 5 year period. The other will be appointed as a Research Associate and must have at least a B.S. degree with demonstrated ability in chemical instrumentation research. Salaries will be commensurate with experience. The presence of the Regional NMR Center and a large NMR research group creates a stimulating environment for NMR work at CSU. Applicants should send a CV to Prof. Jack R. Norton, Instrument Facility Search Committee, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, and should have three letters of recommendation sent to the same address. Review of candidates begins June 15, 1987, and will continue until the position is filled. Colorado State University is an EEO/Title IX employer. Equal Opportunity Office: 314 Student Services Building.

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Range: 90-120MHz
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Switching: 5-20μs
Output: +3 to +10dBm: 50 ohm
Spurious Outputs: −75dBc

Phase Noise: −75dBc, (0.5Hz-15KHz)
Freq. St'd: Oven, TCXO, Ext.
Interface: BCD par. or GPIB
Size: 19″W, 5¼″H, 18″D
Price: $4,400.00*

Other Options:
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Range: 0.1-160MHz
Resolution: 0.1Hz-100KHz (opt.)
Switching: 5-20μs
Output: +3 to +13dBm: 50 ohm
Spurious Outputs: −75dB

Phase Noise: −63dBc, (0-15KHz)
Freq. St'd: Oven, TCXO, Ext.
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Range: 1-250MHz
Resolution: 0.1Hz-100KHz (opt.)
Switching: 5-20μs
Output: +3 to +13dBm: 50 ohm
Spurious Outputs: −70dB

Phase Noise: −63dBc, (0-15KHz)
Freq. St'd: Oven, TCXO, Ext.
Interface: BCD par. or GPIB
Size: 19″W, 5¼″H, 18″D
Price: $6,400.00*

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(or 0-99dB with GPIB)
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or any 10 MHz line (20-140)

PTS 500

Range: 1-500MHz
Resolution: 0.1Hz-100KHz (opt.)
Switching: 5-20μs
Output: +3 to +13dBm: 50 ohm
Spurious Outputs: −70dB

Phase Noise: −63dBc, (0-15KHz)
Freq. St'd: Oven, TCXO, Ext.
Interface: BCD par. or GPIB
Size: 19″W, 5¼″H, 18″D
Price: $7,500.00*

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NMR SPECIALIST

The Department of Chemistry is seeking a specialist in Nuclear Magnetic Resonance Spectroscopy. The position is available immediately, and applications will be accepted until the position is filled.

The position is responsible for operation and maintenance of all Departmental NMR instrumentation, with particular emphasis on new 200 MHz and 400 MHz instruments to be installed this summer. The individual will collaborate with faculty and students in support of specific research objectives leading to scientific publication. Support of instructional programs, including teaching and user training, also is expected.

A Ph.D. in Chemistry is desired. A Master's degree, combined with considerable experience in the operation and maintenance of NMR instrumentation is acceptable. The candidate should have 1-3 years experience in multi-nuclear techniques, including multi-pulse and 2D NMR. Previous chemistry oriented research is highly desired. Previous teaching experience is useful. Salary will be commensurate with experience.

Send CV and three letters of recommendation to:

Search Committee, Department of Chemistry, Acheson Hall, State University of New York at Buffalo, Buffalo, NY 14214.

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Professeur P. J. COZZONE

Marseille, le March 23, 1987
(Received 1 April 1987)

Prof. B.L. SHAPIRO
Department of Chemistry
Texas A and M University
College Station Tx 77843
U.S.A.

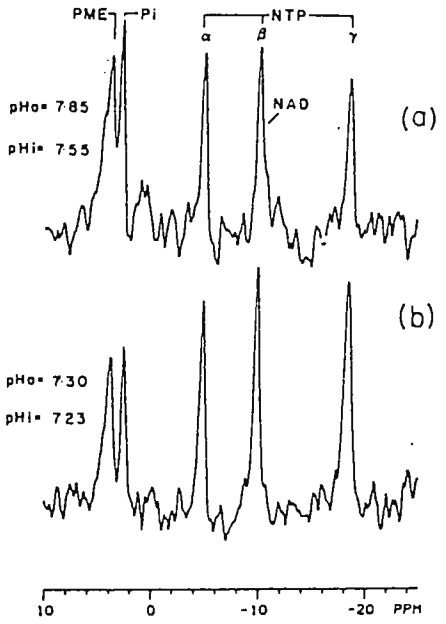
Growth of cancer cell line on microcarrier beads

Dear Barry,

J.P.GALONS, J.FANTINI and ourselves have developed a method allowing the growth of a human colon adenocarcinoma cell line (HT 29) as monolayer on beaded polystyrene (Biosilon) microcarriers. Under optimized conditions, these anchorage-dependent cells became confluent 7 days after seeding and reached a density of 2.8×10^5 cells/cm^2 of microcarrier corresponding to 65% of occupation of the surface available .

The critical parameters that must be controlled in order to obtain optimal cell spread and yield have been identified and are described in a forthcoming paper scheduled to appear in the March-April issue of the International Journal of Cancer. This method is particularly well-suited to obtain cancer cells at an adequate density for recording NMR spectra while preserving their metabolic viability and competence.

The P-31 NMR spectra shown here were recorded at 80.9 MHz on our Nicolet WB-200, without proton decoupling. They correspond to the signals from 3×10^8 cells attached to microcarrier beads, sequestered within the 20 mm NMR tube and perfused at a flow rate of 15 ml/min with defined medium at 37°C containing 15 mM Hepes acid buffered at pH 7.85 (spectrum a) or pH 7.30 (spectrum b). The cells are clearly able to regulate their internal pH and maintain a pH gradient of 0.3 unit across the plasma membrane. Each spectrum corresponds to 1800 FID and 15 min. accumulation.



Sincerely yours,

Patrick J. Cozzone

Paul Canioni

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Prof. B.L. SHAPIRO
Texas A and M University
Department of Chemistry
College Station
TEXAS 77843-3255 ETATS UNIS

RÉF : N : JBR/MFH/9075
V :

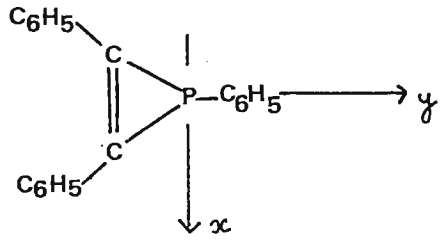
OBJET : Phosphorus Shielding Tensor Determinations

GRENOBLE, le March 25th, 1987
(Received 3 April 1987)

Dear Prof. Shapiro,

After several years with less interest in high resolution and solid state nmr, I am back again in the field. We have been interested in a possible rationale of the σ tensor for a long time. Compounds with unusual bond angles and bond lengths are well suited for such studies. The 1, 2, 3 Triphenylphosphirene where the intracyclic bond angle at the phosphorus is rather small (41.8°) appeared as a good candidate for the σ study. The measured values are given in ppm with respect to the H_3PO_4 85%, positive values at high field.

σ_{xx}	σ_{yy}	σ_{zz}
- 58	28	636



The x or y direction may be exchanged. $\Delta\sigma$ is quite large, however a larger value exists, 1236 ppm in a diphosphene (A. Cowley, University of Texas Austin). In analyzing the spectrum we have been facing a quite difficult problem owing to the extremely large $\Delta\sigma$ value. A simulation of a static powder spectrum gives only rough values. Conversely, the MAS technique used with Herzfeld and Berger

sideband analysis is well suited to the problem. The use of several speeds of rotation enables us to obtain the $\mathfrak{G}$ tensor principal values with quite a good accuracy. Instead of using the Herzfeld and Berger contour plots, we preferred to analyse the spectra directly with a computer program writen on purpose.

Anne-Laure Barra J.B. Robert

UTHSCD/Radiology
Biomedical Magnetic Resonance Center
1323 Record Crossing
Dallas, TX 75235

March 23, 1987
(Received 10 April 1987)

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

Dear Professor Shapiro:

We have the following equipment available:

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- A NT200 console which is not operative due to what appears to be a computer problem. Included in this console are an 1180 CPU, 293A' pulse programmer, two Diablo disk drives, variable temperature unit, spinner air unit, 18 channel RT shim and magnet power supply, miscellaneous probes, and a CPMAS accessory including probes and high power rf amplifier.

Those interested in purchasing any or all of this equipment should contact us at the above address or phone (214) 634-0144.

Sincerely yours,

Ray L. Nunnally, Ph.D. Evelyn E. Babcock, Ph.D

DUKE UNIVERSITY MEDICAL CENTER

Department of Radiology

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

March 26, 1987 (Received 7 April 1987)

Re: NMR Kaleidoscope - New NMR Center

Dear Professor Shapiro:

We report on the kaleidoscope of NMR events currently ongoing at the newly-established Duke NMR Spectroscopy Center. We have just installed and are operating General Electric GN-500 MHz and GN-300WB spectrometers and a Varian XL-300 spectrometer. An eight-member Steering Committee with representation from Biochemistry, Botany, Chemistry, Radiology and the Research Triangle oversees the operating policy and the allocation of NMR time. The Center interfaces in a interdisciplinary manner across the Duke campus in Durham, the Marine Laboratory in Beaufort, and with the Research Triangle area. Spectra A-G are illustrative of current activities.

Spectrum A was obtained with a biochemist and is the 500 MHz ^{1}H NMR spectrum of a molybdenum protein cofactor in DMSO-d_6. Due to the limited material available, this spectrum was run in a cylindrical cavity cell. The hygroscopic DMSO-d_6 and glass vessels were carefully dried and kept dry. The absence of the water signal at 3.3 ppm allows clear observations of cofactor signals in the 3-4 ppm region. Spectrum B was taken together with a chemist and is the 75 MHz ^{13}C NMR spectrum of a synthetic diacid in alkaline D_2O and >1M potassium salt. In standard setup, the extreme pH and high ionic strength of this sample tended to detune the NMR coil. The spectrum was subsequently obtained using a non-standard setup which gave weaker coupling of the sample to the probe. Spectrum C was obtained with a zoologist and is the 120 MHz ^{31}P NMR spectrum of live insects in an aerated state. This system was found to give reproducible ^{31}P spectra over several hours at our aeration conditions.

Spectrum D was obtained with a physician and is the 500 MHz ^{1}H NMR spectrum of an isolated biological fluid. No solvent suppression or field/frequency stabilization using the deuterium lock was used. Spectrum E was studied together with an obstetrician and is the ^{31}P NMR spectrum of fresh human placental tissue. The ^{31}P NMR studies were carried out using a home-built NMR coil on a GE 2.0T CSI horizontal system in the Radiology Department. Spectra F and G were obtained with an opthamologist and are ^{23}Na NMR time course spectra of an eye tissue. The spectra were observed in a two-minute interval with a time gap of 10 min between spectra. The redistribution of Na^{+} signals in this short time gap is a particularly interesting finding.

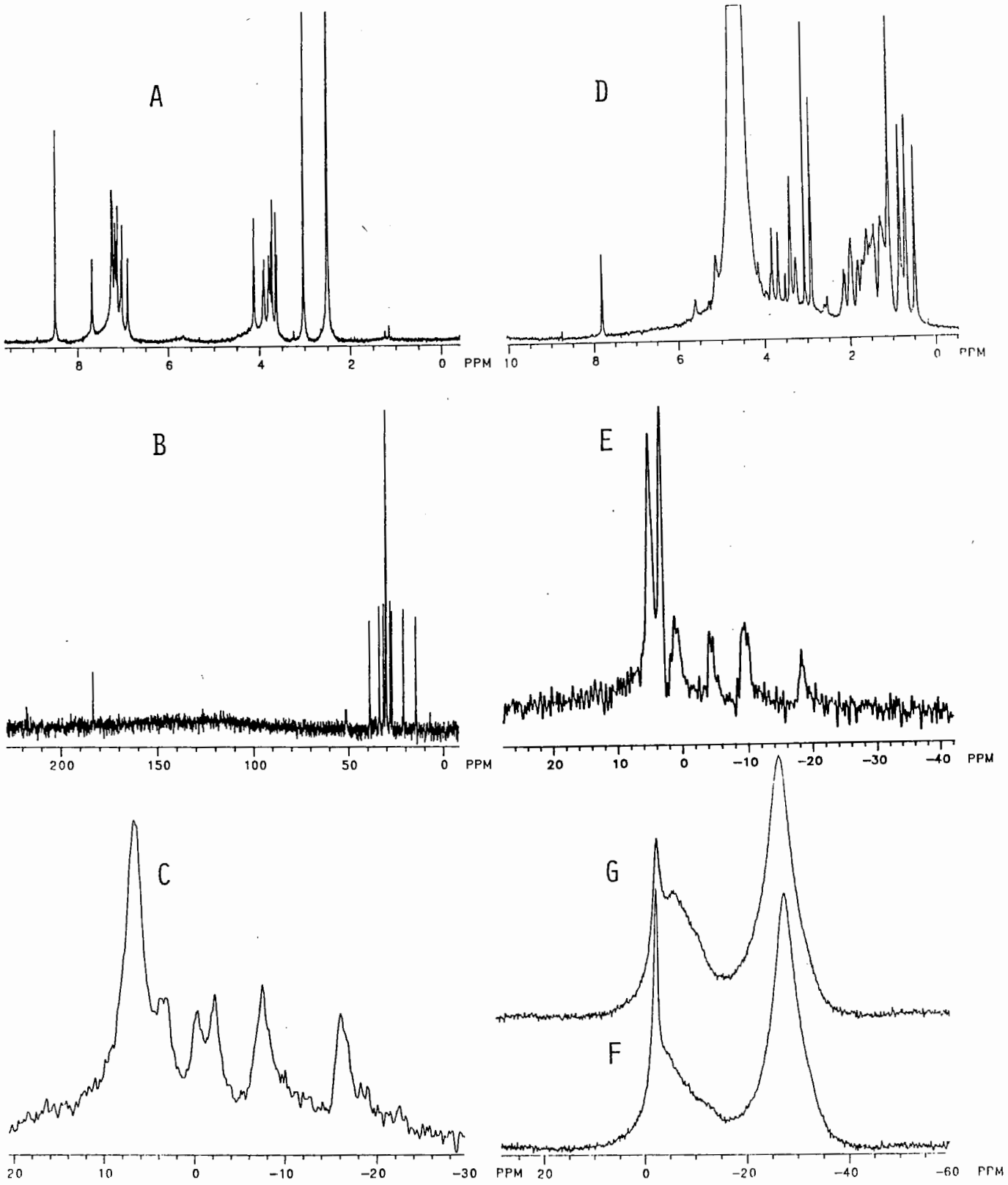
Finally, we would like to invite applications for post-doctoral positions which are regularly available in our NMR Center at Duke.

Sincerely yours,

Leonard D. Spicer
Director

A. A. Ribeiro
Operations Manager

Box 3808 • Durham, North Carolina 27710 • Telephone (919) 684-2711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PPM

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Institute for the Medical Humanities
UTMB Hospitals at Galveston

March 30, 1987
(Received 1 April 1987)

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

TUMOR DETECTION WITH NMR

Dear Barry:

Our JEOL GX270WB spectrometer is alive and well after minor surgery to try to reduce helium loss, and I would like to report some of our recent results in attempting to put the spectrometer to biomedical use. We cannot afford the luxury of fundamental work at this time, but we have been able to address several clinical needs.

The recent report of Fossel et al., New England J. Medicine, 315, 1369 (1986) outlines a procedure for suppression of water in human plasma and measurement of line widths of plasma lipoprotein proton signals in correlation with the presence of diagnosed malignant tumors in patients. The work was conducted with 360 or 400 MHz spectrometers, and the issue of using spectrometers at other fields was discussed.

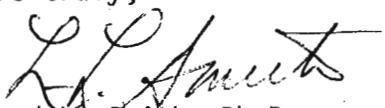
Our present contribution addresses this matter, and we have been able to provide preliminary evidence that the 270 MHz (6.35 Tesla) instrument is fully capable of application to this clinical diagnosis need. A feasibility study conducted by Drs. William Gordon and Ann Wright, Radiation Therapy Department of UTMB, included 18 plasma samples sorted by our proton data into three groups:

Group	No. cases	Average Line Width
1. Normals, no known diseases	4	37.0 ± 2.0 Hz
2. Untreated malignant disease	6	26.4 ± 3.5 Hz
3. Treated malingancy (> 2000 cGray)	8	29.3 ± 3.4 Hz

An additional group of 17 cases with no known health state identified as contributing to line width decrease gave an average line width of 29.9 ± 2.8 Hz. These cases may be at risk if these measurements be validated. For balance, the data of Fossel et al. were 39.6 ± 1.6 Hz for 44 normal cases, 29.9 ± 2.5 Hz for untreated cancer patients (81 cases).

Fossel et al. offered an hypothesis that the state of disorder in plasma lipoprotein particles influence line widths. In a very preliminary test of this concept we examined eight plasma samples for lipoprotein ^{31}P spectra (overnight accumulation, 40,000 scans) that might disclose similar order-disorder influences. However, phosphatidylcholine and phosphatidylethanolamine signals were of unequal intensities and overlapped so as to preclude direct individual line width measurements. Interpolation of the signals to baseline and estimation of line widths for the averaging treatment of Fossel et al. gave average line widths of 36-51 Hz but with no apparent distinction between plasmas from normals and from carcinoma patients. These data and this relatively crude treatment cannot be viewed as definitive disposition of this concept.

Yours truly,



Leland L. Smith, Ph.D.
Professor of Biochemistry

National Center of Neurology and Psychiatry

NATIONAL INSTITUTE OF NEUROSCIENCE
4-1-1 Ogawahigashi, Kodaira
Tokyo 187, Japan
Telephone: (0423)41-2711

March 31, 1987
(Received 7 April 1987)

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

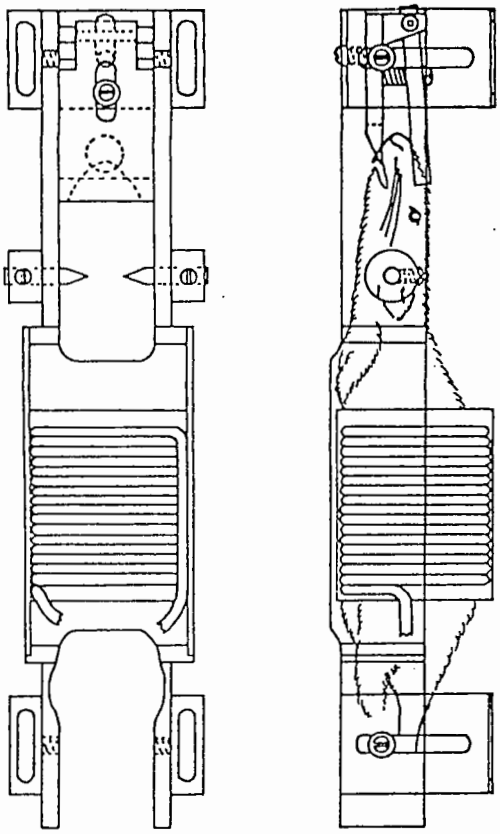
A STEREOTAXIC APPARATUS IN AN NMR PROBE

Dear Prof. Shapiro:

This may be our first contribution to the TAMU NMR Newsletter.

As part of our research program in the area of brain metabolism and dysfunction at the National Institute of Neuroscience, we are interested in development and application of in vivo NMR. Since Ackerman et.al. had introduced a surface coil to measure P-31 NMR of rat brain in 1980, many modifications regarding a coil/probe design have been appeared in the literatures. Very few papers, however, have described an apparatus to hold an animal in the probe body. In fact, some papers still use only tapes to fix the animal in the NMR probe even in a vertical probe configuration probably in a very sophisticated way. In in vivo NMR of brain, this may be one of the most essential part of experiments to obtain reasonably reproducible data.

We have constructed an animal holder made of lucite in the NMR probe which is adopted from a stereotaxic apparatus used in experimental neurobiology for many years(see Figure). The apparatus can be constructed with a little work of plastic mechanics. We can keep an awake rat in the probe of vertical position with the aid of this apparatus at least for several hours without any sign of deterioration of physiological data such as EEG, ECG and blood pressure.



Sincerely yours,

Takashi Ogino, PhD
Director
NMR Research Lab.

Toshio Yano, PhD
Research Associate

The UCLA Department of Chemistry and Biochemistry has an immediate opening for an NMR Spectroscopist in the departmental Instrumentation Facility. Responsibilities will include all aspects of implementation of modern NMR methods in a large variety of chemical and biochemical research, maintenance of NMR hardware and software, and improvement of the hardware, software, and laboratory policies to maximize availability and usefulness of NMR to the research efforts of the department. Primary qualifications are state-of-the-art expertise in NMR spectroscopy and the ability to communicate and relate well with Facility users. Current equipment: AM500, GN500, AF200, WP200, FX90Q. An MSL300 and an AM360 are on order. Interested candidates should send a resume and the names of three references who may be contacted to: Dr. Jane Strouse, Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA 90024. UCLA is an equal opportunity affirmative action employer.

OSU The Ohio State University
Department of Chemistry
120 West 18th Avenue
Columbus, Ohio 43210
Phone 614-292-2251

(Received 7 April 1987)

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

31 March, 1987

DISPA-BASED AUTOMATIC PHASE CORRECTION OF FT/NMR SPECTRA

Dear Barry,

Automatic phasing of FT/NMR spectra continues to pose a vexing problem, particularly when one needs to phase each of a series of spectra from an unattended experiment (e.g., progressive saturation, unknowns from an automatic sample changer, temperature-variation, etc.). Prior phasing techniques include iterative frequency-domain procedures (1,2), or time-domain autoregression analysis (3) requiring prior knowledge of the number of assumed exponentially decaying sinusoids.

Some years ago, we showed that for a perfectly phased Lorentzian line, a plot of dispersion-vs.-absorption (DISPA) gives a perfect circle, tangent to the origin, with diameter along the abscissa (4). Mis-phasing of such a peak by ϕ radians simply acts to rotate the DISPA plot by that same angle. Since no other line-broadening mechanism appears to affect a DISPA plot in this way (5), it is logical to seek a DISPA-based phasing method.

Unfortunately, prior DISPA-based phasing methods either are iterative (6) or can require a large number of points (7), slowing their computational speed. In this contribution, we note that the center of a DISPA circle suffices to determine the phase of a Lorentzian peak. Thus, from as few as three data points per peak, one can locate the DISPA center from the intersection of the perpendicular bisectors of two or more chords of the DISPA circle (Figure 1). We have written Fortran (for Nicolet 1280) and Pascal (for Bruker Aspect 3000) programs to determine the phase for two or more peaks, and then fit the phase spectrum (i.e., phase vs. frequency) to a polynomial in frequency, from which the entire data set may be phase-corrected. The method is rapid--an assembler-based version should provide essentially real-time phasing--and appears to work well even for spectra with relatively poor signal-to-noise ratio (Figure 2). The method requires well-separated peaks, but can be adapted to phase symmetrical multiplets, as for the usual J-coupled high-resolution spin-1/2 case (8). Please credit to account of A. G. Marshall.

Edward C. Craig and Alan G. Marshall

1. R. R. ERNST, J. Magn. Reson. 1, 7 (1969).
2. M. M. SIEGEL, Anal. Chim. Acta 133, 103 (1981).
3. J. TANG, C. P. LIN, M. K. BOWMAN and J. R. NORIS, J. Magn. Reson. **62**, 167 (1985).
4. A. G. MARSHALL and D. C. ROE, Anal. Chem. 50, 756 (1978).
5. A. G. MARSHALL, in "Fourier, Hadamard, and Hilbert Transforms in Chemistry" (A. G. Marshall, Ed.), pp. 99-123, Plenum, New York, 1982.
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7. C. H. SOTAK, C. L. DUMOULIN, and M. D. NEWSHAM, J. Magn. Reson. 57, 453 (1984).
8. E. C. CRAIG, and A. G. MARSHALL, submitted for publication.

(continued on page 41)

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Via this open letter, I personally want to thank you all for your support as is shown by incoming orders for our NMR Sample Tubes. We have thrived and prospered during the past 20 years, **and we shall continue in our efforts to serve you with better quality, lower cost, and faster service.**

If you have any questions, please write or call me, toll-free at 1-800-222-0036. If you have something new that you want us to construct and share with others within the NMR Community -- we shall be glad to discuss it with you.

Sincerely yours,

Mark W. Norell

Mark W. Norell
President

Dedicated to serve the Scientific Community in NMR, Spectrophotometry, and Chromotography.

(continued from page 38)

The Ohio State University

Department of Chemistry
120 West 18th Avenue
Columbus, Ohio 43210
Phone 614-292-2251

31 March, 1987

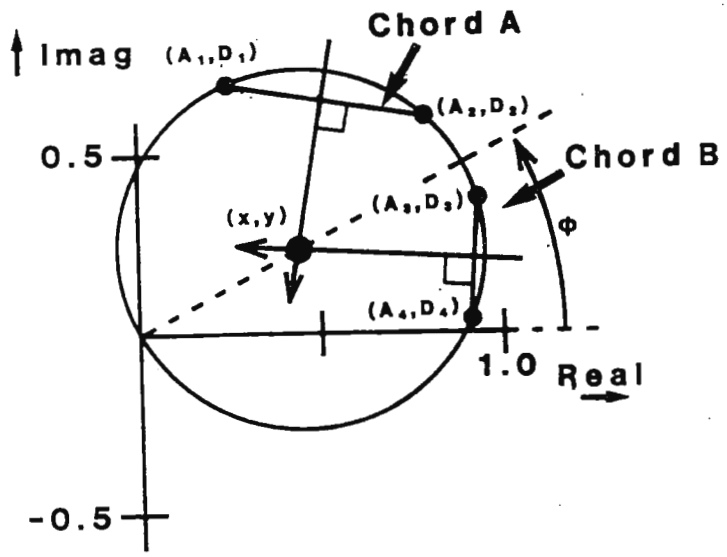


Figure 1. Graphical location of the center of a DISPA circle from the intersection of perpendicular bisectors of two chords.

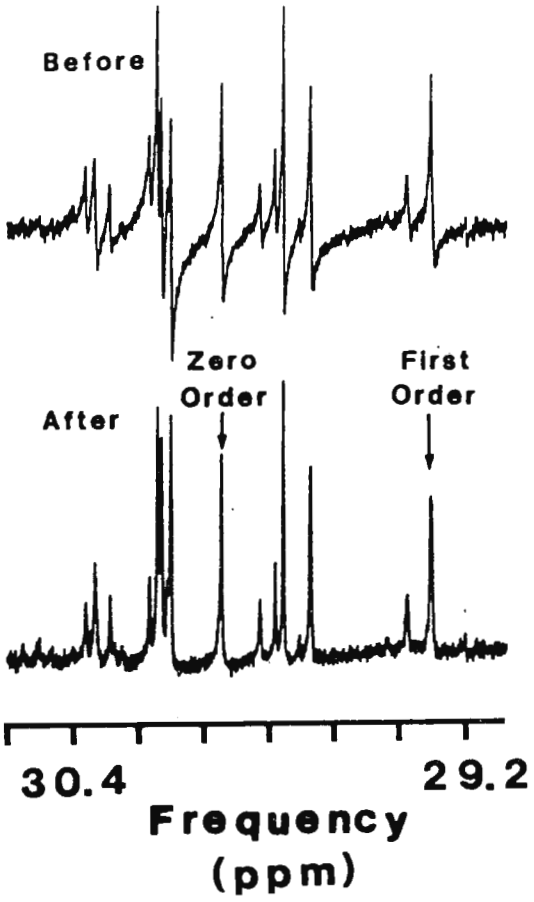


Figure 2. Unphased (top) and DISPA-phased (bottom) proton-decoupled ^{13}C spectra of aqueous saturated sodium dodecyl sulfate. The peaks chosen for zero- and first-order phase correction are indicated.

University of Illinois
at Urbana-Champaign

School of Chemical Sciences
505 South Mathews Avenue

Urbana
Illinois 61801

April 1, 1987
(Received 6 April 1987)

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

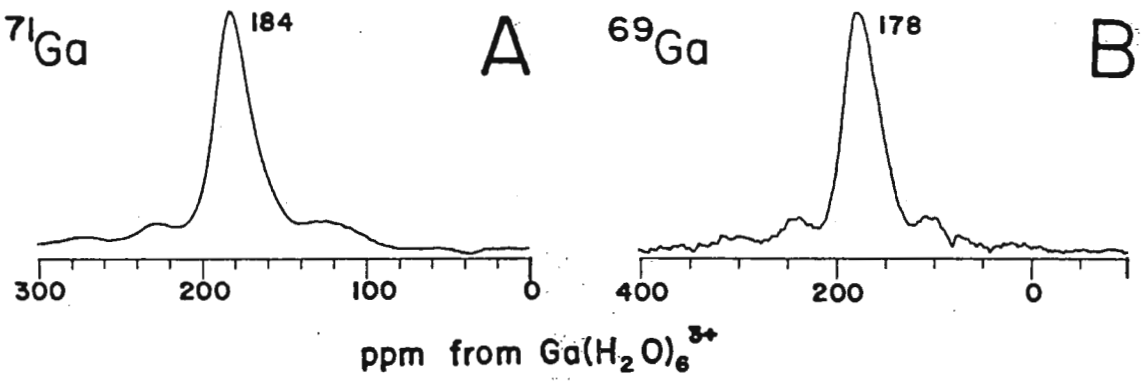
Dear Barry:

Frequency Dependence Study at a Single Magnetic Field Strength

by Using Isotope Pairs

During the study of gallium analog zeolites using solid-state ^{69}Ga and ^{71}Ga NMR, we found a potentially useful new approach to obtaining nuclear quadrupole coupling constant (e^2qQ/h) and isotropic chemical shift (δ_i) values, for non-integral spin quadrupolar nuclei.

We show in the following Figure:



the 11.7 T ^{69}Ga and ^{71}Ga magic-angle sample spinning (MASS) NMR spectra of the gallium analog of sodalite. The observed chemical shifts, δ_{obs}, are at $178._2$ ppm and $183._8$ ppm for ^{69}Ga and ^{71}Ga, respectively. The differences in δ_{obs} are due to the different quadrupole moments and Larmor frequencies of the two isotopes, which cause different amounts of second-order quadrupole induced shifts (δ_{QS}) from the isotropic chemical shift (δ_i). For both ^{69}Ga and ^{71}Ga (I=3/2), the quadrupole-induced shift from the isotropic chemical shift for the central transition of a powder sample undergoing MASS is given by:[1]

$$\delta_{QS}(ppm) = -\frac{10^5}{4}\left(\frac{e^2qQ}{h\nu_o}\right)^2\left(1+\frac{\eta^2}{3}\right)$$

where e^2qQ/h is the nuclear quadrupole coupling constant, ν_o is the Larmor frequency, and η is the asymmetry parameter of the electric field gradient tensor. The values of e^2qQ/h for the two isotopes differ only by the ratio of their nuclear quadrupole moments (Q), because the electric field gradients (eq) felt by the two isotopes are essentially identical. If we assume $\eta = 0$, we can readily determine that for Ga-sodalite the true isotropic chemical shift is 185.6 ppm, and the values of e^2qQ/h are 2.07 MHz and 1.30 MHz for ^{69}Ga and ^{71}Ga, respectively. Although η is unknown, uncertainties in its value cause at most a 15% error in determination of the quadrupole coupling constant, and cause no error in determination of the isotropic chemical shift.

The method has, in suitable cases, advantages over the more conventional field-dependent approach. First, only one magnet is required, although it should be of the highest field strength possible to maximize the spectral signal-to-noise ratio. Second, because lines are narrower at high-field for second-order quadrupolar dominated systems, it is not necessary to spin as fast in the high-field MASS experiment as at low field. We believe that the method may be of use in obtaining e^2qQ/h and δ_i values for other isotope pairs.

Yours sincerely,

Hye Kyung C. Timken Eric

Hye Kyung C. Timken Eric Oldfield

HKCT:EO:kjm

(1) H.K.C. Timken and E. Oldfield, submitted to J. Am. Chem. Soc.

Equipment Available

JEOL FX-90Q for sale. Broad band; 10 mm, 5 mm, and micro inserts. Closed couple heat exchanger. Contact Dr. M. Jane Strouse, Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024, (213) 825-9841.

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(Received 16 April 1987)

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

April 6, 1987
Č.j. 344

Routine Measurement of Fossil Fuel Samples

Dear professor Shapiro,

the instalation of new AM-400 Bruker NMR spectrometer with the sample changer and data station in our laboratory absorbed lot of our time last year. We were very busy to learn all what is necessary for the manipulation with the spectrometer and with spectra. During this time I was also interested in the evaluation of our standard method for quantitative NMR analysis of fossil fuel samples, which we developed for our Tesla FT NMR spectrometer operating at 25 MHz for ^{13}C NMR spectra.

First, we measured the relaxation times of different crude oils and coal derivatives (liquid samples). Some of them we studied seven years ago, so we could compare original and new data. For most samples we have found no important difference in the T_1 values measured at 25 MHz and 100 MHz respectively. For example, the relaxation times of methyl carbon atoms at 14,5 and 14,1 ppm of the pipe line crude oil sample were found the same at both frequencies. The others T_1 differ of about 10%. The addition of the relaxation reagents $Cr(acac)_3$ decrease the relaxation times so that using of the concentration of about 0.025 mol/l gives the T_1 values bellow 1 s. On the base of these results the acquisition parameters for the old and new equipment can be used the same (eg. flip angle close to 90°, repetition time 10 s) and the systematic error due to the

relaxation times and NOE ought to be supposed similar.

Second, I compared the random errors of the integration due to the base line and phase corrections. For the aromaticity f_a of crude oil I obtained the relative standard deviation % $\bar{s}$ in the range from 6-7% at 25 MHz and 2-3% at 100 MHz respectively. According my opinion the main decreasing of % $\bar{s}$ is connected with the application of five parameters base line correction, which is a standard of Bruker software, as well as the comfort with the manipulation with spectra on the screen.

Third, the difference of sensitivities of both spectrometers gives the possibility to measure 40-50 samples of crude oil derivatives every week at AM-400. We were able to measure the same number of samples with Tesla equipement during two month. We found, that the using of data station for a such amount of data is necessary for economical utilization of new spectrometer.

Sincerely yours,

Milan Hájek

Prague Institute of Chemical
Technology
Czechoslovakia

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16th April 87
(Received 21 April 1987)

Prof. B.L. Shapiro
TAMU NMR Newsletter
Texas A & M University
Department of Chemistry
College Station, Texas 77843-3255
U.S.A.

HOHAHA spectra in H_2O without solvent irradiation

Dear Professor Shapiro,

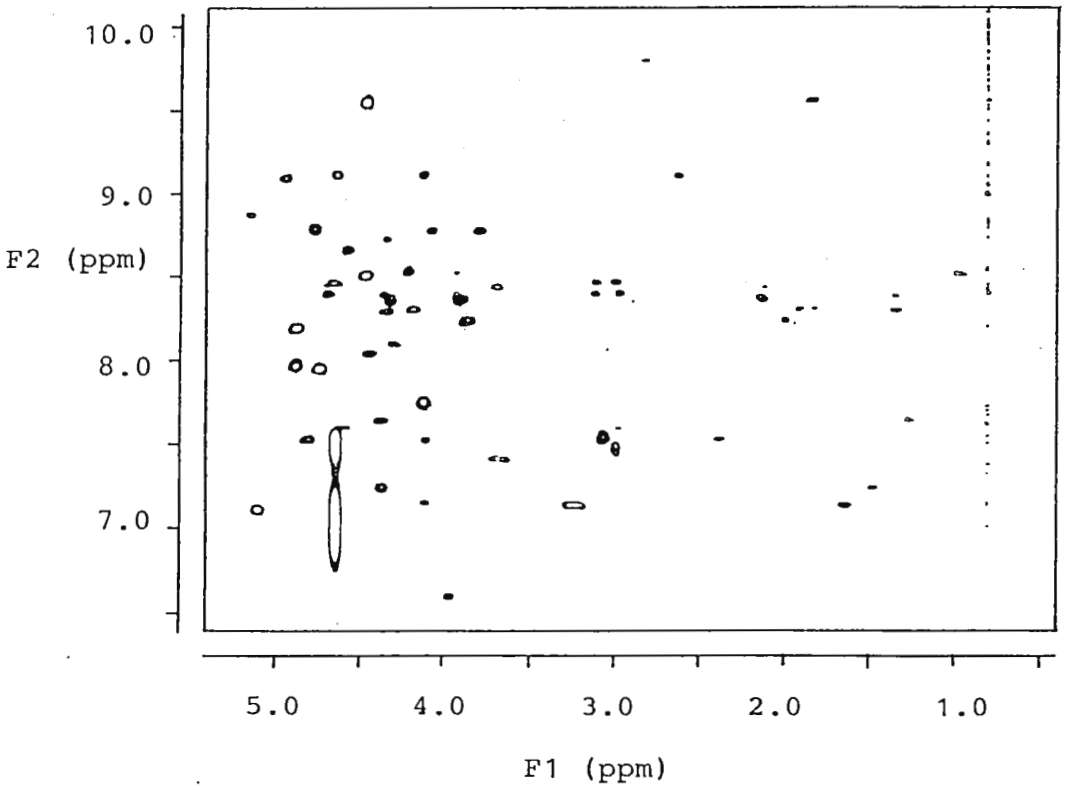
Recording spectra in H_2O comprises an essential part of the analysis and assignment of protein NMR spectra. Conventionally spectra used to demonstrate through-bond connectivities (e.g. COSY, DQF-COSY, HOHAHA, etc...) are recorded with irradiation of the H_2O resonance. This necessarily results in bleaching of the NH-CαH cross peaks involving CαH resonances close to or at the same position as the water resonance. Recently Sklenar & Bax (J. Magn. Reson. in press, 1987) have reported a simple method for getting round this problem by the addition of the sequence 90_x-H-d-90_x-τ-90_{-x}-Δ-90_ϕ-2τ-$90_{-\phi}$-Δ at the end of either the $MLEV17_y$ sequence in the case of the HOHAHA experiment or following the last 90^o pulse in the case of a COSY or DQF-COSY experiment. The meaning of the symbols in the sequence is as follows: H is a homospoil pulse, d a recovery delay from the homospoil, 90_x-τ-90_{-x} the jump return sequence, Δ a short delay 100 μs at the beginning and end of the refocussing echo sequence 90_ϕ-2τ-$90_{-\phi}$ in which the phase ϕ is cylced in the exorcycle manner. A 45 ms HOHAHA spectrum of potato carboxypeptidase inhibitor (7 mM) in 90% H_2O recorded using this water suppresion read pulse is shown in the accompanying figure. As is evident, the quality of the

spectrum is good and cross-peaks at and close to the water resonance are clearly detectable. Thus this technique promises to be very useful in the sequential assignment of protein NMR spectra.

Yours sincerely,

G. Marius Clore Angela M. Gronenborn

Figure legend. HOHAHA spectrum of 7 mM potato carboxypeptidase inhibitor in 90% H_2O. The digital resolution is 6.88 Hz/point and the spectrum was recorded in approximately 12 hours.



CHEMAGNETICS, INC.
208 Commerce Dr., Fort Collins, Colorado 80524
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April 3, 1987
(Received 17 April 1987)

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

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Sincerely,

Joseph A. DiVerdi, Ph.D.
Senior Scientist

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INSTITUTE FOR CANCER RESEARCH ■ 7701 BURHOLME AVENUE ■ PHILADELPHIA, PENNSYLVANIA 19111
215/728-6900

April 23, 1987
(Received 27 April 1987)

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

Re: Equipment Available

Dear Professor Shapiro:

We are planning to sell our NT-300 WB NMR spectrometer (except the magnet). The system was delivered in mid-1983 and is in perfect working order. It exceeds all of the installation performance specifications. The console includes full broadbard capabilities from 5 to 200 MHz plus ^{19}F and ^{1}H. It also has:

1. A 1280 computer, 293C pulse programmer and raster (color) display,

2. CDC 'Hawk' disk drive,

3. ^{1}H, CIDNP and GN series broadband probes (10 mm).

A separate data station consisting of a 1280 with array processor, raster display and CDC 'Hawk' disk drive is also available for sale.

Persons interested in purchasing this equipment may write to us at the above address or can contact me (215-728 3631) or Dr. Josh Wand (215-728-3123) by phone.

Sincerely yours,

Robert W. Dykstra

RWD/m
cc: J. Wand

344-50

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Professor B.L. Shapiro,
Department of Chemistry,
Texas A&M University,
College Station,
Texas 77483,
U.S.A.

19th March,1987
(Received 30 March 1987)

12mm NMR ACCESSORIES AVAILABLE

We have a set of 12mm NMR accessories which we would like to dispose of. This consists of the following items:

(1) A set of 8 sealed NMR Reference Samples originally supplied with a Varian XL100/15 specrometer.

(2) 40 12mm O.D. NMR tubes (Wilmad 514-7PP grade) of which half have never been used.

(3) 4 0.85ml capacity microcells.

(4) 2mm O.D. TMS reference capillaries with spacers.

(5) PFTE vortex suppressors, sample reducers and plastic NMR tube caps.

If you would like to have these accessories, please contact Mike Kinns at Pfizer Central Research,Ramsgate Road,Sandwich, Kent CT11 9NJ, U.K.

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Professor Bernard L.Shapiro
Texas A & M University
Chemistry Department

College Station, TX. 77843
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V/Réf. N/Réf. Lausanne, le 14.4.1987

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Prof. Barnard L. Shapiro
Department of Chemistry
Texas A&M University
College Station TX 77843-3255

March 24, 1987
(Received 2 April 1987)

Dear Prof. Shapiro:

Re: CP/MAS OF Graphite-Containing Samples

Happy St. Patrick's Day! In the course of celebrating my Irish heritage, I should dispel some common blarney about the perils of graphite.

I agreed a few months ago to apply CP/MAS ^{13}C NMR to an external customer's composites of graphite fibers held together with a synthetic polymer. The object was to determine the effects of manufacturing process variables on the structure of the cured synthetic. Before I got started on the work, though, I began hearing that graphite, a good electrical conductor, raises hell in CP/MAS experiments. To wit, that:

- the external magnetic field induces eddy currents in graphite with sufficient back force to prevent the sample from spinning;
- high-power pulses across a conducting sample cause arcing in the probe; and
- a fat graphite signal will dominate the spectrum and obliterate the polymer peaks, if I were to observe anything at all.

Recommended fixes for these difficulties were to dilute the sample with Epsom salt and to operate at lower CP power. As these samples were two-thirds graphite, diluting and running at low power meant that accumulation times could get up to a few days; not a thrilling prospect.

I began by running one sample as a powder diluted with two parts Epsom salt by weight. The mixture spun as easily as any normal sample, there was no probe arcing, and the spectrum obtained after 16 hr showed no obvious graphite peak at about 130 ppm. Delightfully, an undiluted composite powder produced the same results with improved S/N ratio. Thus, it seems that the only problem graphite causes (in these materials, at least) in CP/MAS experiments is to dilute the polymer of interest. Having no proton content to speak of, graphite tends not to be observed by cross polarization. In fact, a difference spectrum obtained by subtracting a neat cured polymer spectrum from a composite spectrum shows a small, broad graphite peak centered at about 125 ppm whose area corresponds to only one-fourth of the total composite intensity, while graphite comprises three-fourths of the total carbon in the composite.

By way of detail, the intact composites had electrical resistivity of 30-60 ohm/cm. They were reduced to powders in a Spex shatterbox. Spectra were acquired on a GE S-100 spectrometer, with spinning speeds of 3000 rps and CP γH_1 levels of about 45 kHz.

The confidentiality of the work does not allow me to send spectra.

Respectfully yours,

Larry Amos

Larry W. Amos

LWA:ckw2C/0324/a80

LH **University of Houston**

College of Pharmacy
4800 Calhoun Road
Houston, Texas 77004
713.749.3476

Department of Medicinal Chemistry and Pharmacognosy

April 20, 1987 (Received 21 April 1987)

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

Decoupling Modulations in Long-Range 2D NMR Spectra

Dear Barry:

Anticipating your "reminder" which came in today's mail... We've been working recently with long range heteronuclear chemical shfit correlation and thought that some of the results that we've obtained may be of interest to readers of the Newsletter.

Long range heteronuclear chemical shift correlation has become an important technique for structure elucidation and spectral assigment. Many groups are performing the experiment by simply optimizing the conventional heteronuclear chemical shift correlation experiment for long range couplings. While this approach assuredly works, there is a major pitfall: one bond modulation, which may lead to the loss of anticipated long range responses. Unfortunately, there does not seem to be a general appreciation of the problem. Several groups have been concerned with the effects of modulation induced by the directly attached proton when magnetization is transferred long range to a protonated carbon. Freeman and co-workers[1] were the first to express this type of concern followed by Reynolds and colleagues.[2] A recent communication from this laboratory[3] experimentally confirmed one bond modulation for a simple model aromatic compound. Other work which is now in press has documented the ability of a BIRD pulse located midway through the Δ_2 evolution time to suppress one bond modulations.[4,5]

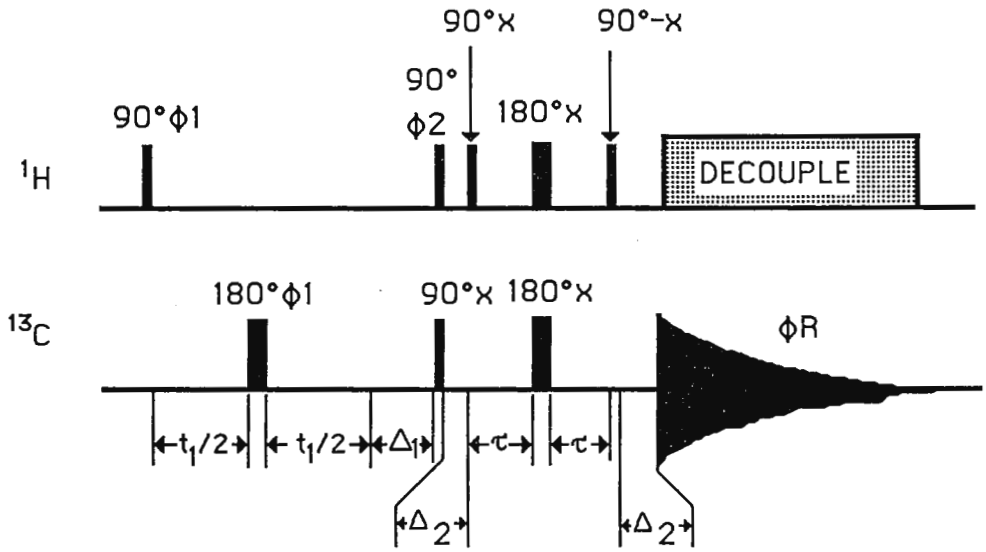
Modulation of response intensity may be predicted using the equation:

$$I = \sin(\pi\Delta_1 {}^{LR}J_{CH}) \sin(\pi\Delta_2 {}^{LR}J_{CH}) \prod \cos(\pi\Delta_2 {}^{1}J_{CH}) \times \cos(\pi\Delta_2 {}^{LR'}J_{CH}) \quad [1]$$

where I = response intensity; Δ_1 and Δ_2 are the magnetization transfer delays as normally employed in heteronuclear chemical

shift correlation; $^{LR}J_{CH}$ = the long range delay being studied (exploited?); $^{1}J_{CH}$ = the one bond coupling constant of the carbon to which magnetization is being transferred; $^{LR'}J_{CH}$ = other long range coupling constants.[3] The heavily modulated curve plotted for the C2H6 coupling pathway of 3,4-diaminopyridine in the figure is derived using [1] and takes into account $^{3}J_{C2H6}$, $^{1}J_{C2H2}$ and $^{4}J_{C2H5}$.

Insertion of the bird pulse midway through Δ_2 gives the modified pulse sequence shown below

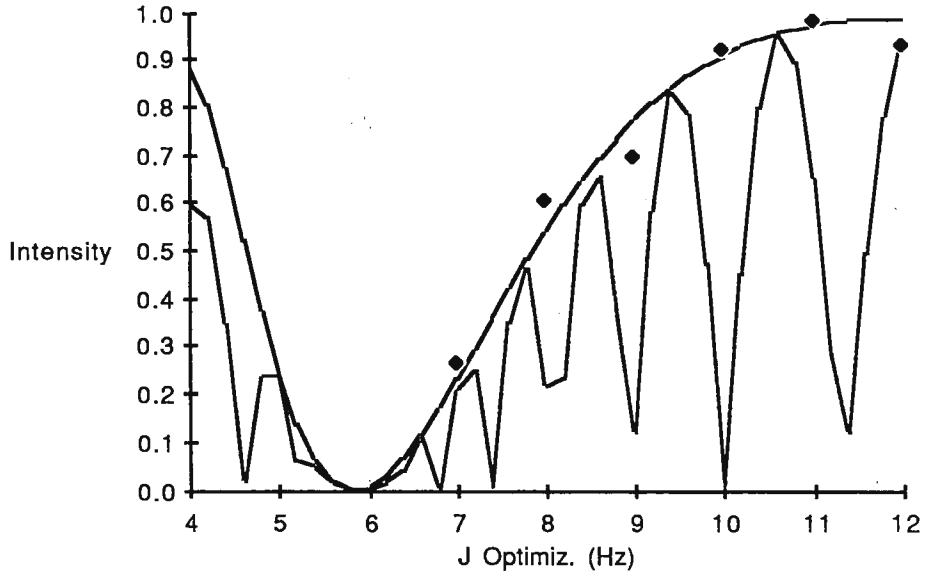


ϕ_1 0202 2020 ϕ_2 0123 2301 ϕ_R 0321 0321

which simplifies [1] to give [2][4,5] where response intensity, I, is given by the expression:

$$I = \sin(\pi\Delta_1 {}^{LR}J_{CH}) \sin(\pi\Delta_2 {}^{LR}J_{CH}) \prod \cos(\pi\Delta_2 {}^{LR'}J_{CH}) \qquad [2]$$

where the terms are defined as above. The smooth curve shown in the figure below was calculated using [2]. Experimentally determined points for a range of optimization values obtained using the pulse sequence shown above are superimposed over the smooth curve.



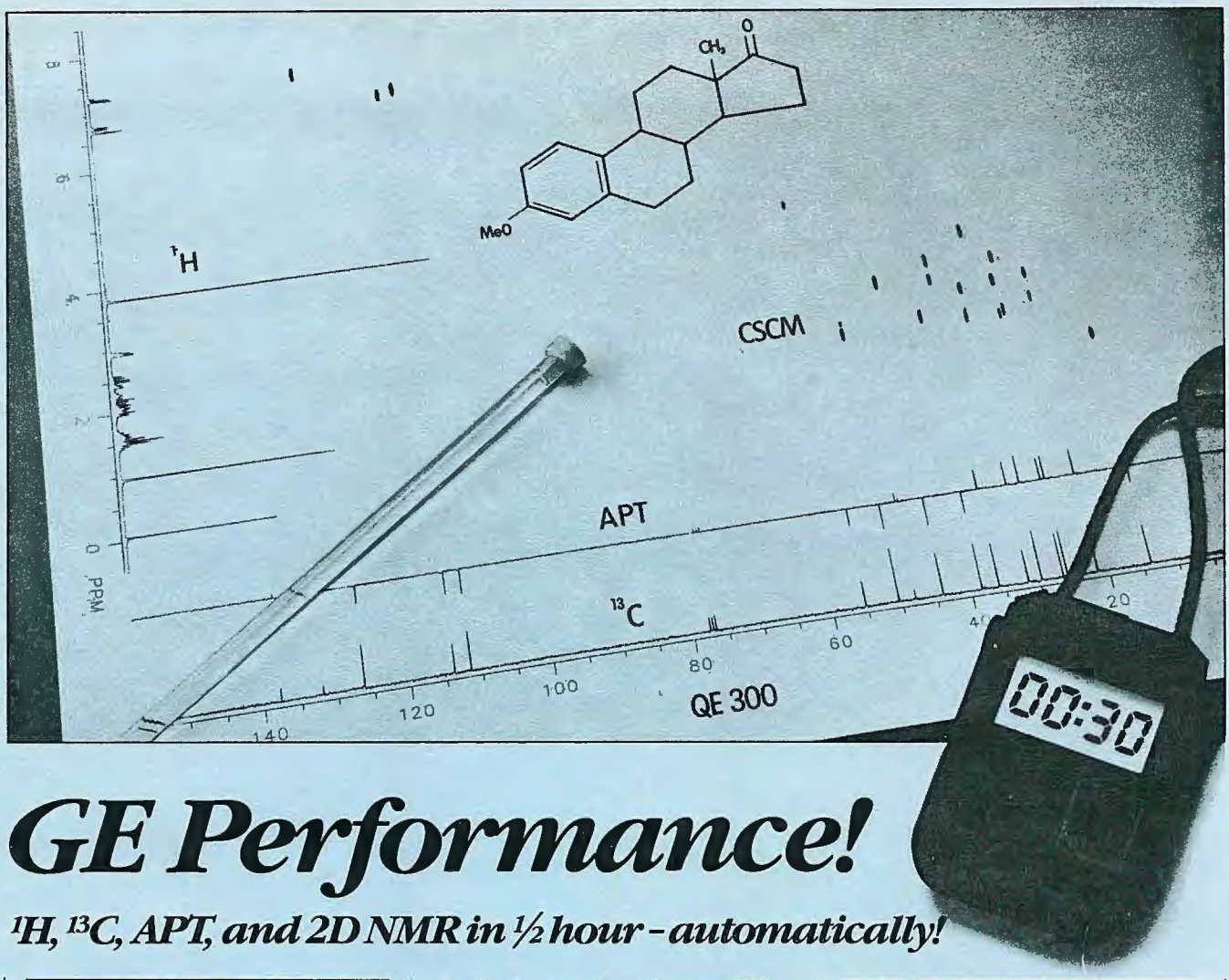
From the graphical presentation, it should be quite apparent that the inclusion of the BIRD pulse midway through the Δ_2 delay effectively "decouples" the undesirable one bond modulation. Modified pulse sequences containing a BIRD pulse midway through Δ_2 provide a more reliable means of obtaining long range correlations eliminating the concern of losses of responses due to the one bond modulation problem.

Sincerely,

Gary E. Martin Andrew S. Zektzer

References:

1. C. Bauer, R. Freeman and S. Wimperis, J. Magn. Reson., **58**, 526 (1984).
2. W.F. Reynolds, D.W. Hughes, M. Perpick-Dumont and R.G. Enriquez, J. Magn. Reson., **63**, 413 (1985).
3. M.J. Quast, A.S. Zektzer, G.E. Martin and R.N. Castle, J. Magn. Reson., **71**, 554 (1987).
4. A.S. Zektzer, B.K. John, R.N. Castle and G.E. Martin, J. Magn. Reson., **72**, in press (1987).
5. A.S. Zektzer, B.K. John and G.E. Martin, Magn. Reson. Chem., **25**, in press (1987),



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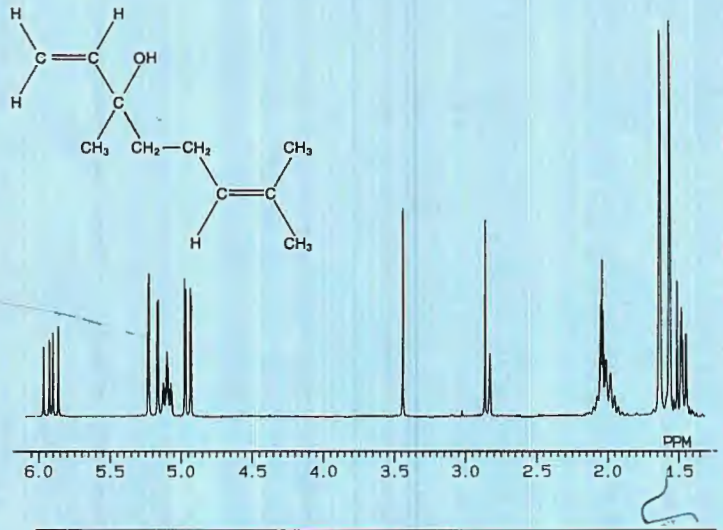

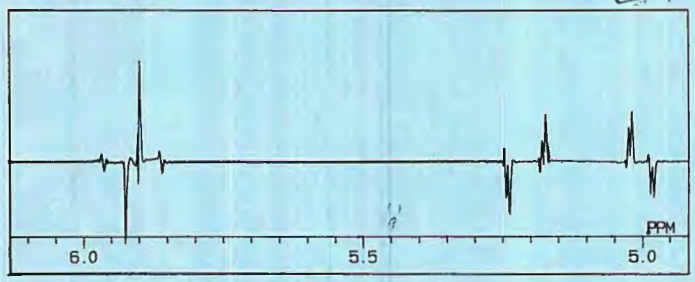

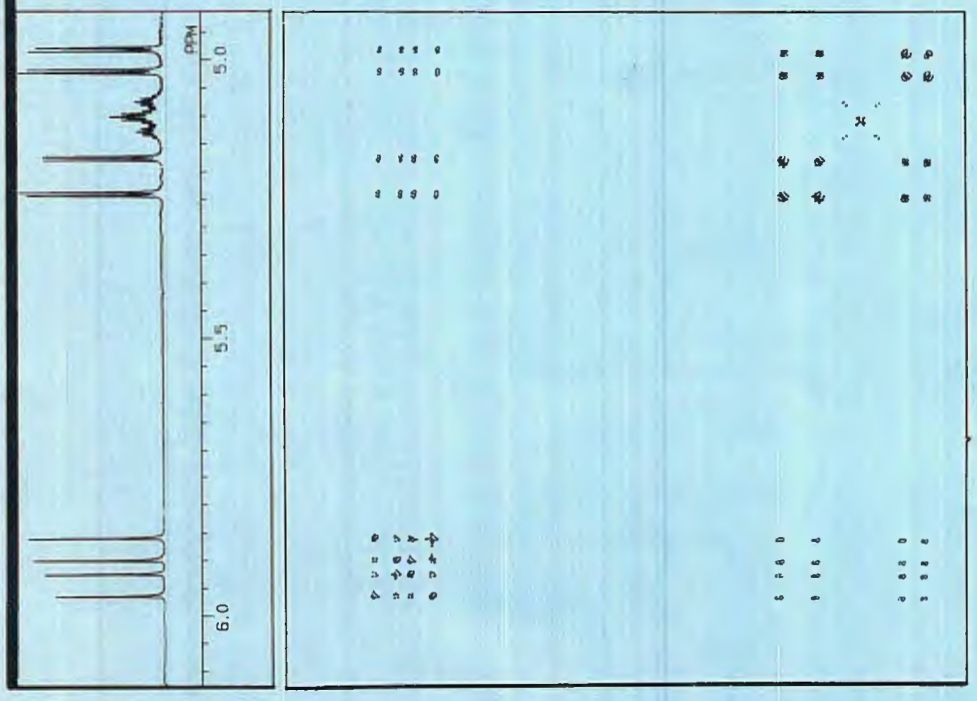

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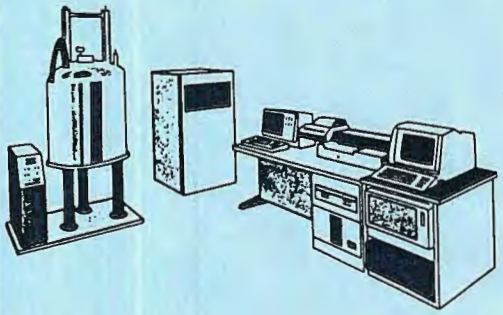

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