TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 345

June 1987

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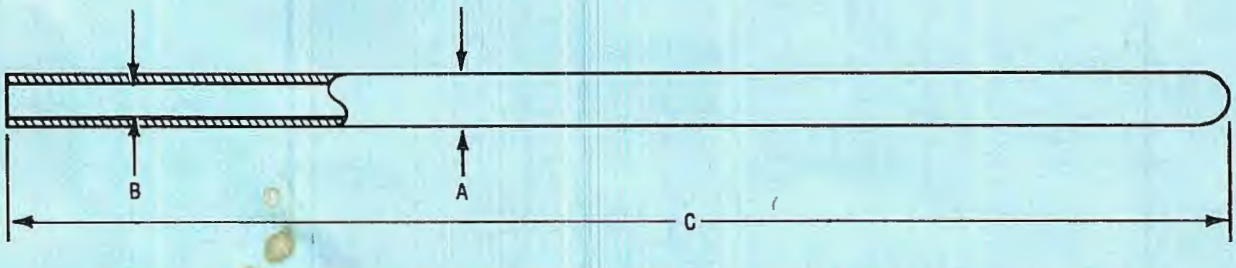

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540-PPT	Royal Imperial					0.001″	0.0005″
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AUTHOR INDEX ------- TAMU NMR NEWSLETTER, NO. 345, JUNE 1987

ADVERTISERS

FORTHCOMING NMR MEETINGS

In Vivo NMR Spectroscopy Summer School - August 31-September 5, 1987; University of Orleans, Orleans, France. See page 23 of Newsletter #343, April 1987, for additional information.

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.

Magnetic Resonance Spectroscopy for Clinicians - October 18, 1987; San Francisco, California; University of California Medical Center, San Francisco, California; For registration information, call (415) 476-5808.

1987 Materials Research Society, Fall Meeting - Nov. 29 - Dec. 5, 1987; Boston Marriott Hotel, Boston, Massachusetts. Short course on NMR Spectroscopy - Wednesday, December 2. Course Instructor: James P. Yesinowski (Cal Tech). For further details, contact: Materials Research Society, 9800 McKnight Road, Suite 327, Pittsburgh, Pennsylvania 15237.

Fritz Haber International Workshop on Modern Techniques in Magnetic Resonance - December 13-17, 1987; Weizman Institute of Science, Rehovot, Israel; See page 7 of Newsletter #341, February 1987, 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. 347 (August) --------- 31 July 1987

No. 348 (September) ---- 28 August 1987

DIASONICS
MRI DIVISION
533 Cabot Road
South San Francisco, CA 94080
(415) 872-2722

April 21, 1987 (Received 27 April 1987)

Subject: Artifact Management in 2D (or more) NMR

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

Dear Dr. Shapiro:

I would like to describe a trick that I have been using in imaging which I think has application to other 2D and 3D NMR experiments. It is a relatively simple idea, but I've not seen it published yet. Fourier imaging experiments are plagued with all of the usual artifacts in 2D NMR. However, the usual remedy of cycling all of the RF pulse phases requires more signal averaging than is desired in imaging and probably in other experiments on protons.

A typical 2D-imaging sequence looks like Figure 1. The image obtained after 2DFT has a bright dot in the center from receiver DC-offset and a streak across the middle of the t1 (phase-encoding) direction from a residual FID off of the nominal 180 degree pulse. No amount of flip-angle adjustment can remove the signals from the edges of the selective pulse profile. The spatial encoding in the t1 domain occurs prior to this FID, thus it is found in the center line.

The usual remedy is to phase alternate the 180-degree pulse and combine (add) pairs of signals; or better, alternate the 90 degree pulse phase and subtract which also removes the receiver d.c. offset. My suggestion is to phase alternate the 90 degree RF pulse, but go on to the next step in the t1 dimension without averaging. The result is that the desired signals are modulated at the Nyquist frequency in w1 and aliased. The d.c. offset and FID from the 180 degree pulse remain at their old location; w1=0. By "rolling" the 2DFT by N/2 lines one regenerates the "normal" image (or spectrum) but with the artifacts along the edge in the w1 dimension.

This is useful for imaging since the edge of the data array is almost always uninteresting. I believe that there are some other experiments, J-spectra for example, where this might be useful to remove spurious signals from the J=0 region.

As a demonstration, I've included an image of a test object in Figure 2. Figure 2a is the result without phase modulation, 2(b) is with modulation but before rearrangement of the output of the 2DFT, and 2(c) is the full treatment.

Sincerely yours,

David M. Kramer

Mailing address: UCSF-Radiologic Imaging Laboratory
400 Grandview Drive
South San Francisco, CA 94080

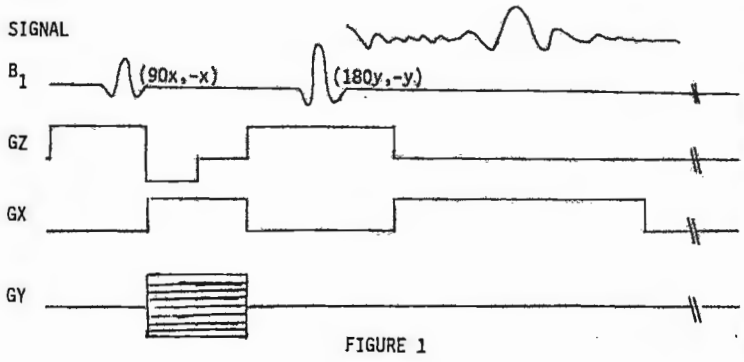
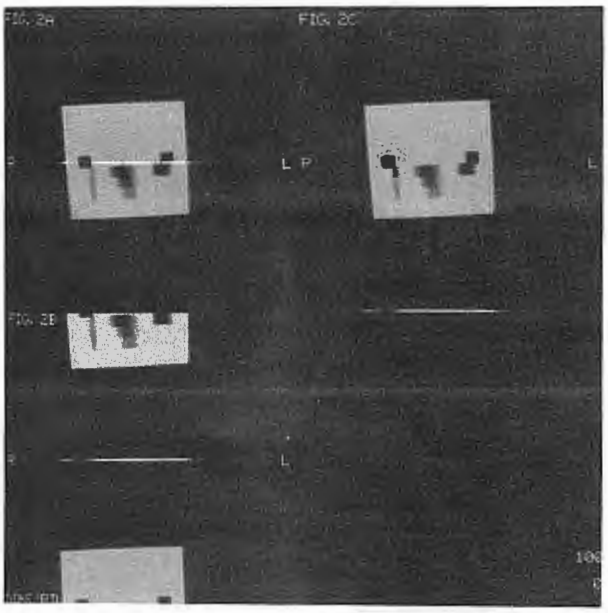


FIGURE 1



Notice

Invoices for subscriptions, etc., for the TAMU NMR Newsletter for the subscription year October 1987 - September 1988 will be mailed one month later than usual this year. We expect to mail our invoices for the year in question on or about August 3.

B.L. Shapiro

Pfizer
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Direct line (0304) ------

22nd April, 1987.
(Received 1 May 1987)

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

Dear Professor Shapiro,

Testing Automatic Sample Handling Using Aluminium Placebos

We have recently added a sample autochanger to our QE-300 spectrometer at Sandwich. This machine is operated on an open access self-service basis and is used to acquire ~70 ^{1}H spectra/day, and a selection of ^{1}H, ^{13}C and 2D spectra under automation at night. During the shakedown period for the autochanger, we could not afford to have the spectrometer down during the day, but we wanted to check the sample handling of the pneumatic system when powered by a small compressor.(a)

We employed a local engineer(b) to turn down 50 aluminium alloy rods to the dimensions shown in Figure 1 (i). These aluminium placebos are approximately the same mass as an 8"/5 mm o.d. tube half filled with $CDCl_3$ (~7 g.) When set in the spinner as shown (Figure 1 (ii)) and loaded into the autochanger carousel they perform, for handling purposes, as a real sample.

A simple MACRO program is used to load, spin and eject the test samples with the time delay to mimic data acquisition. This system allows us to make changes to the air supply and distribution and to check the operation of the autochanger, without the danger of a partially ejected glass tube sample being crushed and the fragments contaminating the probe.

(a) JUN-AIR 12-50DL.
(b) Mr. D. Pugh c/o K.S.I.P., University of Kent, Canterbury.

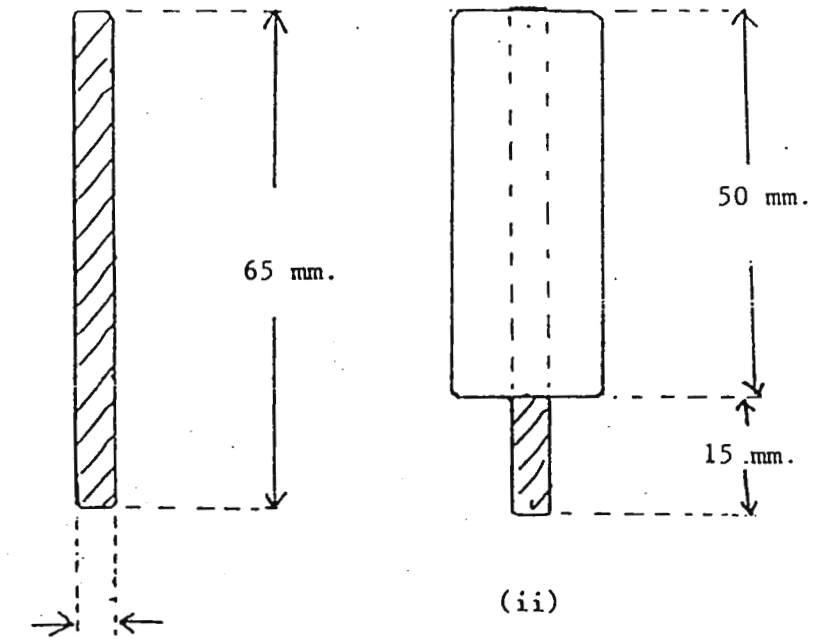
Yours sincerely,

Michael J. Newman

M. J. Newman
Analytical Chemistry Department

(Please credit this contribution to the Pfizer Central Research, Sandwich, account, Dr. D. V. Bowen).

Figure 1



Sandia National Laboratories

Albuquerque, New Mexico 87185

April 22, 1987
(Received 25 May 1987)

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

Dear Barry:

Trifluoromethylated Cyclopropane and Cyclopropene
C-F Coupling Constants

As part of my recently completed thesis (University of Illinois, with Professor J. C. Martin, now at Vanderbilt University) I found it necessary to measure the C-F coupling constants of several known (**3-6**) and previously unknown trifluoromethylated compounds (**1,2,7**). Despite the large amount of 19F NMR work in the literature, there is comparatively little data on 13C spectra of fluorinated compounds, especially with respect to C-F coupling constants. The chart on the next page is a summary of the coupling constants that were measured and demonstrates the utility of the constants in assigning 13C spectra.

In general, 1J CF3 couplings in which the CF3 is attached to a saturated cyclopropane/cyclopropene carbon are greater than 272 Hz, whereas 1J CF3 couplings in which the CF3 is vinylic are smaller, always less than 272 Hz. The 2J couplings follow a reverse pattern, saturated less than 47 Hz, unsaturated (with the exception of the ketenimine) greater than 50 Hz. The 3J coupling constants are typically small (~2-3 Hz) and difficult to resolve.

Finally, the molybdenum complex is arguably a metallatetrahedrane based on a combination of structural and NMR data. Further discussion/data/syntheses of these molecules (including a less hazardous synthesis of **6**) will soon be submitted for publication (Organometallics, manuscript in preparation).

Sincerely,

Paul A. Cahill

Paul A. Cahill
Division 1811

P.S. Here at Sandia we now have an 200 MHz IBM instrument for routine solution work and a wide bore 200 MHz Chemagnetics/Nicolet/Nalorac/Cryomagnet system which is used primarily for solids.

References:

3: Oakes, T. R.; David, H. G.; Nagel, F. J. J. Am. Chem. Soc. **1969**, 91, 4761-4765.

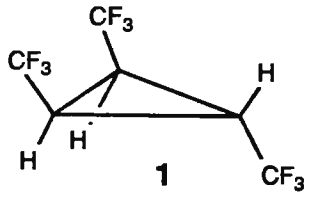
4,5: Birchall, J. M.; Burger, K.; Haszeldine, R. N.; Nona, S. N. J. Chem. Soc., Perkin Trans 1 **1974**, 2080-2086.

6: Grayston, M. W.; Lemal, D. M. J. Am. Chem. Soc. **1976**, 98, 1278-1280.

Sandia National Laboratories

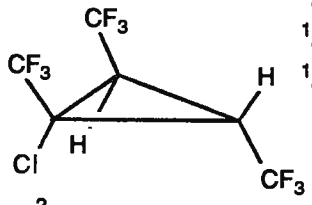
Albuquerque, New Mexico 87185

All ^{13}C Spectra at 50 or 75 MHz



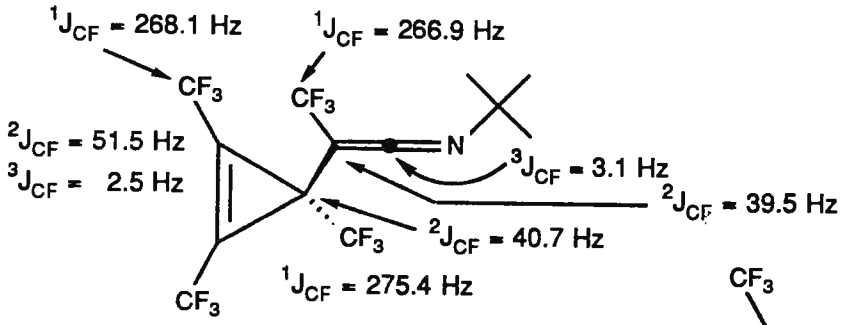
1

$^1J_{CF}$ = 274.0 Hz
$^2J_{CF}$ = 34.7 Hz

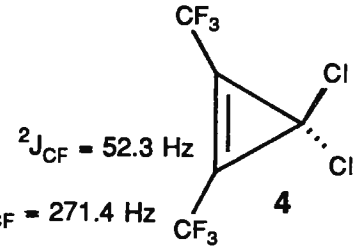


2

$^1J_{CF}$ = 274.7 Hz
$^1J_{CF}$ = 274.7 Hz
$^1J_{CF}$ = 275.7 Hz
$^2J_{CF}$ = 39.8 Hz, CH
$^2J_{CF}$ = 42.5 Hz, CH
$^2J_{CF}$ = 42.6 Hz, CCl

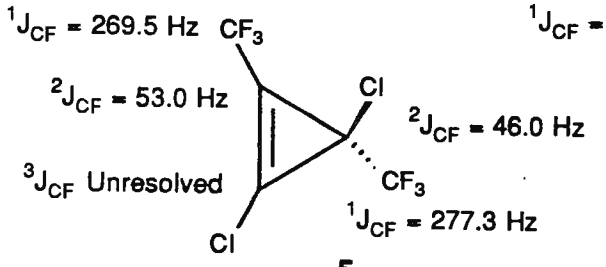


3



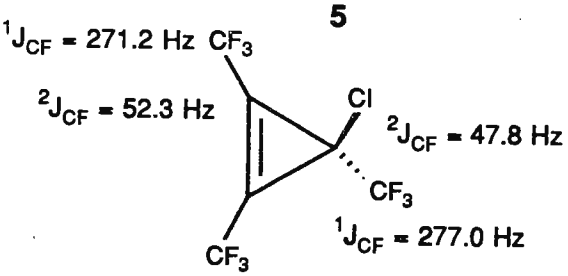
4

$^2J_{CF}$ = 52.3 Hz
$^3J_{CF}$ = 2.2 Hz
$^1J_{CF}$ = 271.4 Hz



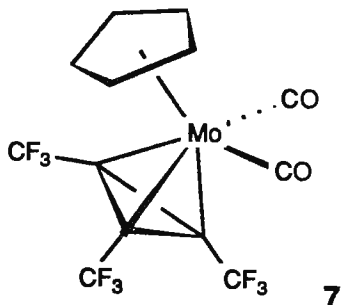
5

$^1J_{CF}$ = 269.5 Hz
$^2J_{CF}$ = 53.0 Hz
$^2J_{CF}$ = 46.0 Hz
$^3J_{CF}$ Unresolved
$^1J_{CF}$ = 277.3 Hz



6

$^1J_{CF}$ = 271.2 Hz
$^2J_{CF}$ = 52.3 Hz
$^2J_{CF}$ = 47.8 Hz
$^1J_{CF}$ = 277.0 Hz



7

$^1J_{CF}$ = 267.0 Hz
$^2J_{CF}$ = 51.4 Hz
ring carbons equivalent at room temperature

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Fysische Chemie
De Boelelaan 1083
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The Netherlands

Professor Dr. B. L. Shapiro
Department of chemistry
Texas A & M University
College Station
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uw kenmerk	uw brief van	ons kenmerk	datum	bijlage(n)
		CM/EWB/ETJN	May 8,1987 (Received 15 May 1987)	

onderwerp

Dipolar Couplings in High Resolution NMR Spectra.

Dear Dr. Shapiro,

It is usually assumed that anisotropic spin interactions, like dipolar or quadrupolar couplings, do not modify NMR spectra of normal liquids and solutions. Their effects may, however, become detectable by virtue of a small nett alignment of the molecules, due to the action of the magnetic field of the spectrometer on the anisotropic magnetic susceptibility of these molecules. Indeed, the phenomenon of magnetic field induced alignment in NMR has been well studied (See: E.W. Bastiaan, C. MacLean, P.C.M. van Zijl and A.A. Bothner-By, in: "Annual Reports on NMR Spectroscopy", (Ed.: G.A. Webb), vol.19, p.35 (1987), in press).

For protons, direct magnetic dipole-dipole interactions may show up in the spectra. Their magnitude is proportional to the molecular susceptibility anisotropy, depends quadratically upon the magnetic field strength and varies with the inverse cube of the internuclear distance of the coupled spins. At ^1H frequencies of 500 MHz or less, dipolar couplings D can hardly be resolved and merely cause line broadening. In favourable cases, however, they should be detectable.

Consider for example fluorene (fig.1). The resonance of the CH_2 group is expected to be a doublet with a line splitting of 3D/2. From the susceptibility anisotropy of fluorene, the splitting can be estimated: it is about 0.25 Hz at a proton frequency of 500 MHz. Under normal

(continued on page 11)

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.... or, as most likely the case is
.... **because Norell is taking business away from them due to its superior product quality and Wilmad has no way of combating it other than by downgrading Norell in their advertising campaign???**

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 8)

conditions, the CH_2 line width exceeds 1 Hz (solvent: acetone-d_6), due to interferences of small indirect couplings with the aromatic protons. The usual decoupling at one frequency only is not sufficient in this case and the splitting remains indetectable.

In order to remove the masking of the CH_2 doublet, fluorene containing deuterons at the aromatic positions was synthesized. The indirect couplings are then drastically reduced by a factor of $\gamma_H/\gamma_D \approx 6.5$, if not removed completely by self-decoupling, caused by rapid quadrupolar relaxation of the deuterium spins. Now the CH_2 line width is about 0.85 Hz and by using resolution enhancement, a splitting of 0.30 Hz is found (fig.2).

This illustrates that when proton spectra are recorded at sufficiently strong fields and proper precautions (e.g. decoupling or, like in the present case, deuterium incorporation) are taken into account, dipolar couplings can be determined. The extra fine structure in the spectra is helpful in peak assignments; also information concerning the molecular geometry or magnetic susceptibility anisotropies can be obtained.

Sincerely,

E.T.J. Nibbering E.W. Bastiaan C. MacLean

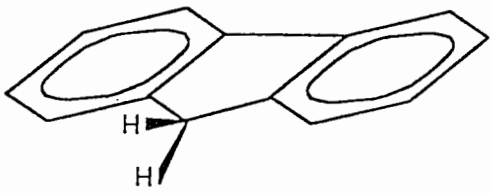

Fig.1: Fluorene

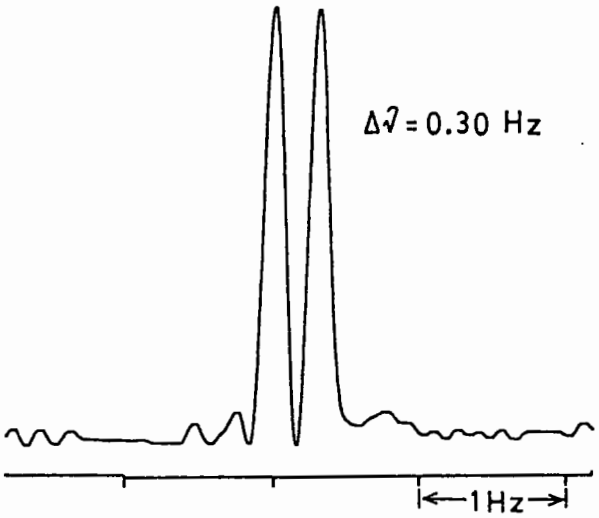

Fig.2: The CH_2 resonance in the 500 MHz proton NMR spectrum of fluorene (resolution enhanced).

AT&T Bell Laboratories

600 Mountain Avenue
Murray Hill, NJ 07974-2070
201 582-3000

April 27, 1987
(Received 6 May 1987)

Transfer of Spectra from a Bruker Spectrometer Computer to a Mainframe Data System.

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

Dear Professor Shapiro,

We describe here a method to transfer spectra from an Aspect 2000A computer on a Bruker CXP-200 spectrometer to a departmental mainframe (or data station) with a UNIX operating system for curve-fitting and further processing. For the number of spectra we transfer (~10/week), this procedure is convenient and inexpensive, as it uses a widely available AT&T 6300 PC already present in our lab, rather than an Ethernet interface or other dedicated hardware. A similar procedure could be written for other commercial spectrometers and other mainframe operating systems.

We use the AT&T PC in a terminal emulator mode to transfer data between the incompatible ADAKOS and UNIX environments. The microcomputer runs the SIMTERM terminal emulator (copyright 1982,1984, Jim Holtman and Eric Holtman, 35 Dogwood Trail, Randolph, NJ 07869) and executes a PASCAL program on the Aspect via the channel B serial interface. After matching word length (7 bits) and parity (none), the data rate on this channel was increased to 9600 baud to speed transfers.

The PASCAL program run from the AT&T PC terminal (see Appendix) causes the Aspect to print the contents of a data file within a specified channel range. These values are captured by the terminal emulator into a disk file by typing "ALT/C" before the listing begins. After each list concludes, the disk file is closed with a second "ALT/C". After all desired files are transferred, the AT&T PC is connected to the mainframe, again in terminal emulator mode with appropriate communication settings, and Kermit (or other file-transfer protocol) is used to upload the files. (For example, in a UNIX environment, one may "vi" a new file, enter the insert mode ("i"), and then dump the file from the AT&T PC by typing "ALT/D". An "escape" concludes the transfer.)

We have found this procedure convenient for occasional transfer of moderately sized (200-1000 points) portions of spectra. With modest changes in the PASCAL listing program, transfer of imaginary components, or of entire

files, is also possible. An additional benefit of the terminal emulator is the availability of a high-speed terminal, which allows for rapid file manipulation in ADAKOS, and permits simultaneous access to the spectrometer by two workers.

Thatcher W. Root D. C. Douglass T. Michael Duncan

Appendix: Source code for PASCAL program to print selected portions of Bruker data files.

```
        PROGRAM OUTPUT;
CONST
     SECSIZE=256;
VAR
        D:ARRAY[0..SECSIZE] OF INTEGER;
        I,J,K,BLOCKIN,LOW,HIGH,NN,SHIFT:INTEGER;
        F1: FILE;
        W1:STRING;
BEGIN
        WRITE('FILE NAME ? '); READLN(W1);
        WRITE('FIRST CHANNEL ? '); READLN(LOW);
        WRITE('LAST CHANNEL ? '); READLN(HIGH);
        WRITE('DIVIDE BY ? '); READLN(NN);
        RESET(F1,W1);
        BLOCKIN:=2*LOW DIV SECSIZE;
        SHIFT:=2*LOW MOD SECSIZE;
        I:=0;
        J:=BLOCKREAD(F1,D[I],1,BLOCKIN);
        K:=0;
                I:=SHIFT;
                WHILE K <= HIGH-LOW DO
                   BEGIN
                      WRITE(D[I] DIV NN:8);
                      K:=K+1;
                      I:=I+2;
                      IF I >= SECSIZE THEN
                        BEGIN
                           I:=0;
                           BLOCKIN:=BLOCKIN + 1;
                           J:=BLOCKREAD(F1,D[I],1,BLOCKIN);
                        END;
                   END;
END.
```

UNIVERSITÉ DE LAUSANNE

INSTITUT DE CHIMIE ORGANIQUE

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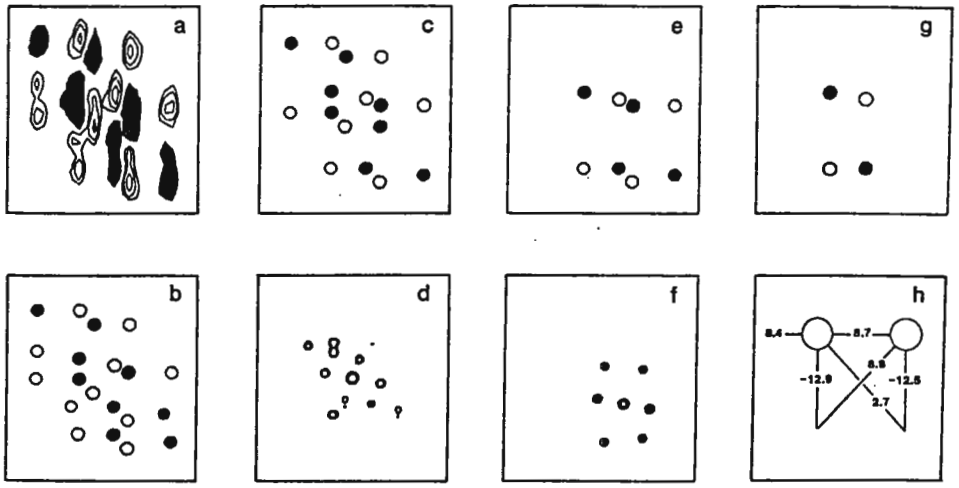
(Received 11 May 1987)

Pattern Recognition in COSY

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

Dear Dr Shapiro, 4th May 1987

We have recently used a new approach to pattern recognition to identify the 7-spin system of D-proline in a z-filtered COSY spectrum (1) of cyclo-(L-Pro-L-Pro-D-Pro), previously investigated by Kessler et al.(2). Figure 1 shows how the procedure works on the experimental cross-peak multiplet $\gamma^{cis}{}_{\leftrightarrow}{}_{\delta}{}^{cis}$ in D-proline:



(a) original multiplet; (b) plot of extrema. The active coupling is determined as the distance between antiphase pairs of points that appears the greatest number of times in each dimension. (c) Rectified multiplet after imposing C_2 symmetry and after insertion of missing corners of antiphase rectangles; (d) contour plot of "symmetry map", with amplitudes S(i,j) proportional to the number of data points in (c) that fulfill C_2 symmetry about the point i,j. The highest peak in this symmetry map corresponds to the center of the multiplet, while the distances in ω_1 and ω_2 between the two next-lower symmetrically-disposed peaks correspond to passive splittings. (e) Reduction of the multiplet by elimination of a pair of passive splittings; (f) and (g) results of second recursion. (h) Resulting fragment of the coupling network. The information contained in 11 such fragments can be put together in the manner of a jig-saw puzzle to give the topological diagram and the numerical estimates of Figure 3.

Yours sincerely

Marjana Novič

Geoffrey Bodenhausen

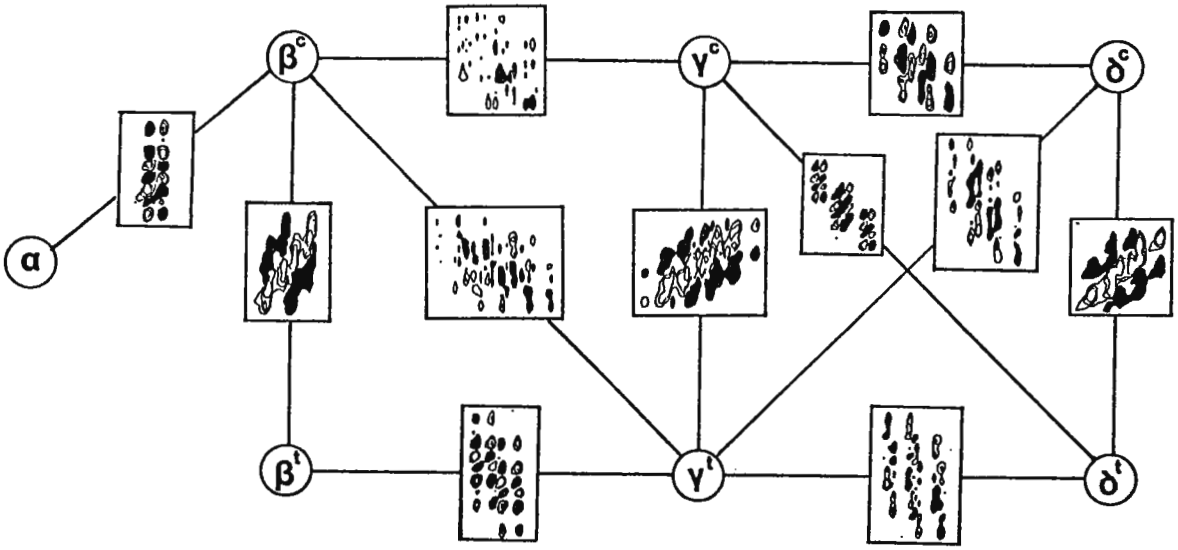


Figure 2. Experimental multiplets taken from a z-COSY spectrum of cyclo-(L-Pro-L-Pro-D-Pro). All 11 multiplets associated with D-Pro are shown, drawn onto a schematic representation of the coupling network.

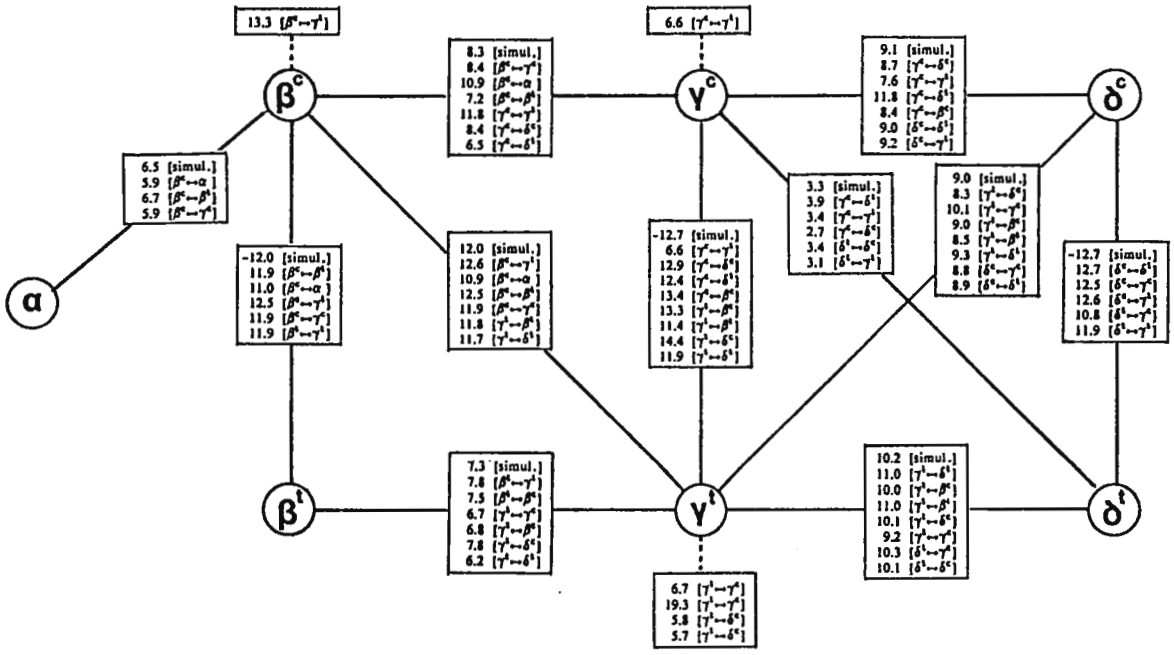


Figure 3. The output of the analysis is overdetermined, since each multiplet yields several values for passive J couplings. The origin of the data is given in squared brackets: the values labeled [simul] are taken from the simulations of Kessler et al.(2). All other values result from our automated analysis. Passive and active couplings have been grouped so as to minimize inconsistency; some values that could not be fitted to any other J coupling may be connected hypothetically to further protons (dashed lines). The numerical accuracy should be compared with a digital resolution of 1.7 Hz/point in both dimensions of the spectrum.

References

1. H.Oschkinat, A.Pastore, P. Pfändler and G. Bodenhausen, J. Magn. Reson. 69, 559 (1986).

2. H. Kessler, W. Bermel, A. Friedrich, G. Krack, and W. E. Hull, J. Am. Chem. Soc. 104, 6297 (1982).

University of Arkansas for Medical Sciences

4301 W. Markham
Little Rock, Arkansas
72205-7199

April 24, 1987
(Received 27 April 1987)

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

Title: ^{119}Sn CPMAS NMR OF Tin Compounds

Dear Barry:

In collaboration with Richard G. Parker and Anthony M. Mazany of BF Goodrich, and Tom Early of GE NMR, we have obtained high resolution ^{119}Sn CPMAS spectra at 33.56 MHz for a variety of organotin compounds. After the early, initial report by Lippmaa(1) and coworkers, only a few short reports by Harris and coworkers recently have appeared (2-4). We found that tetracyclohexyltin, which has a linewidth of about 10 Hz and a cross-polarization time of several hundred microseconds, is a good compound for finding the Hartmann-Hahn match. The magic angle on our Andrew geometry setup was adjusted using dibutyltin oxide ($\Delta\sigma$=737ppm), the spectrum of which is shown in Figure 1 at MAS speeds of 4.7 and 2.3 kHz(chemical shift reference, tetramethyltin). The spectra in Figure 1 suggest a single environment for tin in the solid, which is consistent with what is known about the solid-state structure of this compound.

Figure 2 shows the ^{119}Sn CPMAS spectrum of diethyltin dichloride. The isotropic pattern consists of two, relatively broad resonances of intensity ratio 1:1.5. Because there is only one environment for Sn in the crystal and for other reasons, we attribute this pattern to the effect of the quadrupolar ^{35,37}Cl nuclei on the Sn-Cl dipolar coupling. The spectrum at 111.9 MHz, for which the two-peak pattern almost collapses to a single peak, confirms this interpretation. A similar low-field spectrum was seen for triphenyltin chloride, although the high-field spectrum of this latter compound revealed additional structure.

Tin-119 chemical shift amisotropies for the compounds we have examined ranged from about 40 ppn for tetraphenyltin to 1100 ppm for polymeric di(n-octyl) tin maleate. The full study will appear in J. Magn. Reson. in the near future.

Sincerely,

Rich

Richard A. Komoroski, Ph.D.
Associate Professor of Radiology and Pathology

(continued on page 19)

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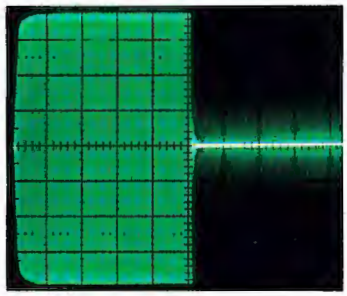
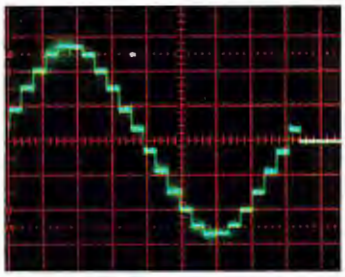
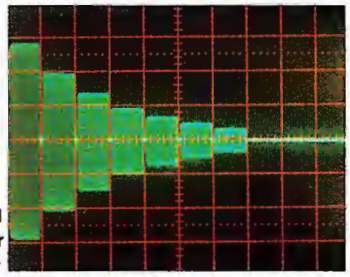




15° phase shift through 360°. ►



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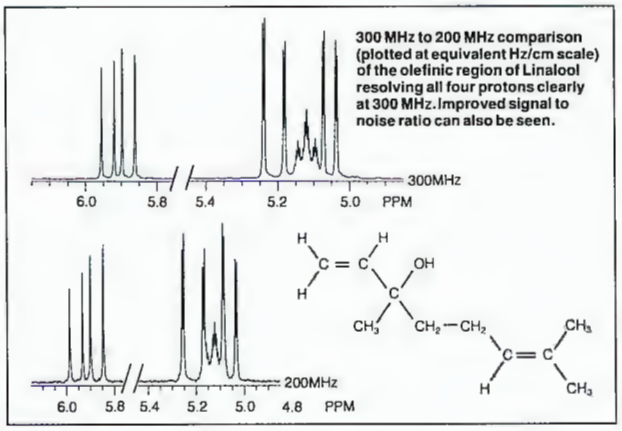

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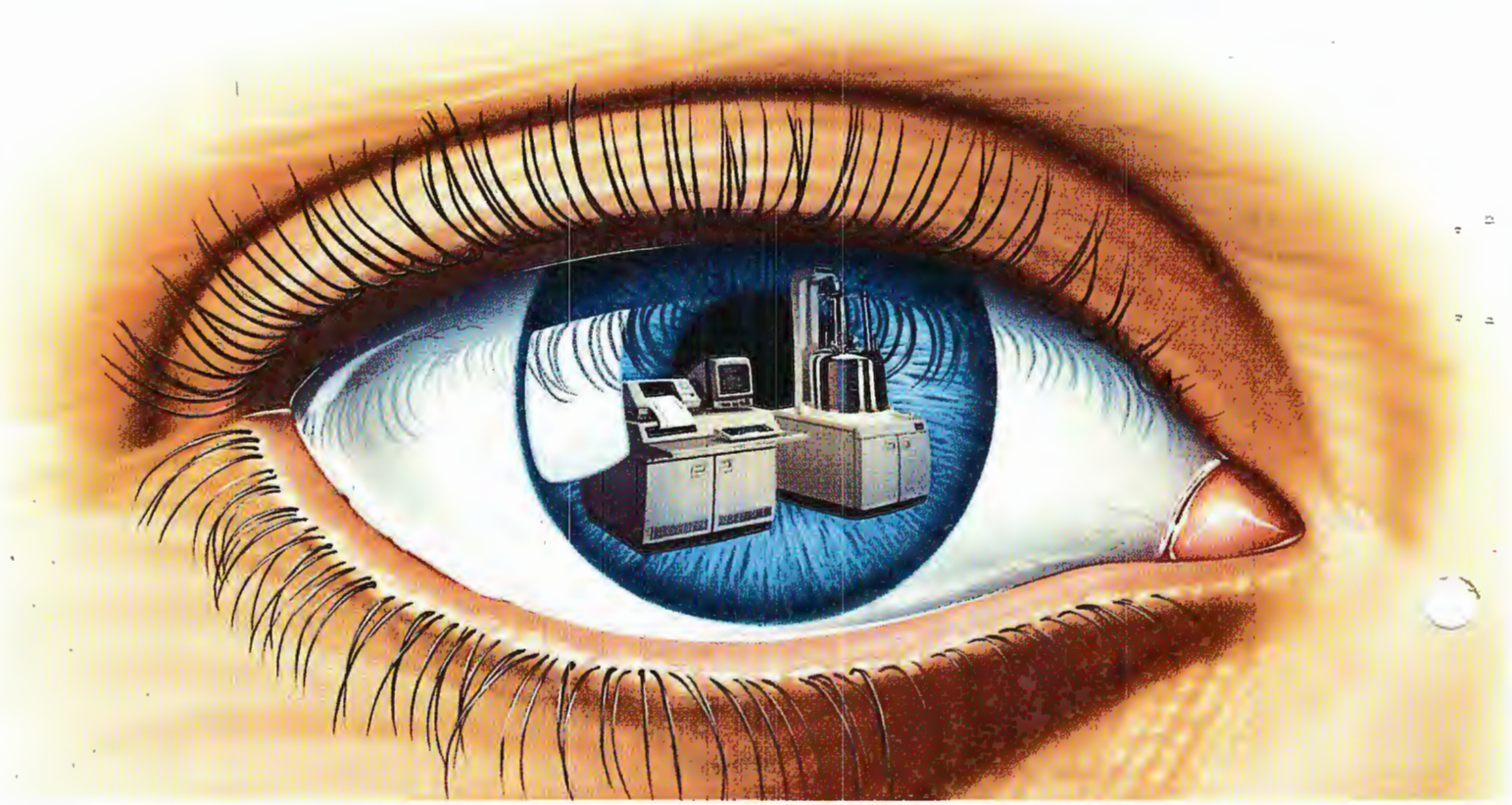

(continued from page 16)

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2. R.K. Harris, K.J. Packer, and P. Reams, J. Magn. Reson. 61, 564(1985).

3. R.K. Harris, K.J. Packer, and P. Reams, Chem. Phys. Lett. 115, 16(1985).

4. R.K. Harris, T.N. Mitchell, and G.J. Nesbitt, Magn. Reson. Chem. 23, 1080(1985).

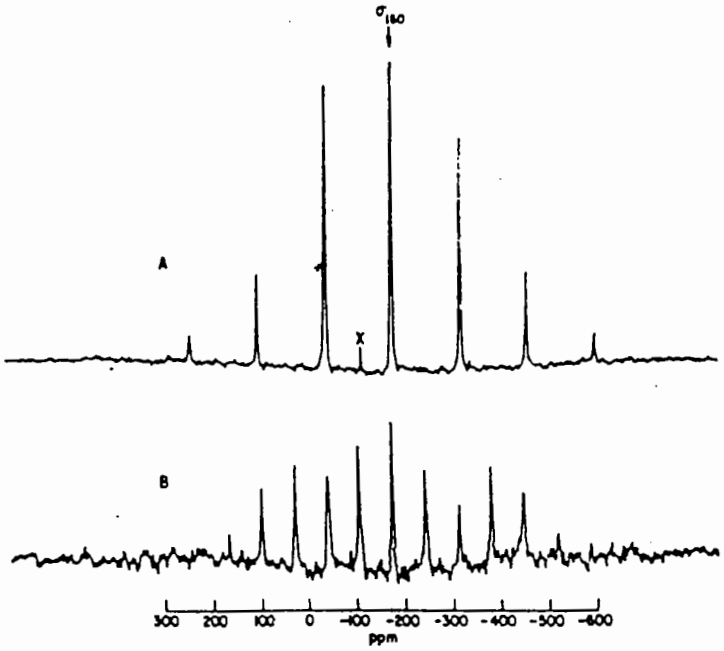

Figure 1

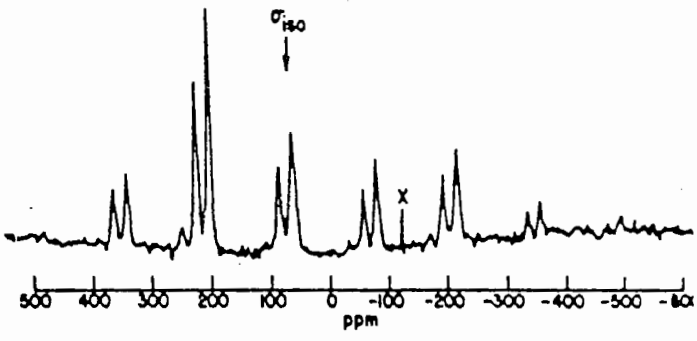

Figure 2

345-20

ICI Chemicals and Polymers Group
PO Box No 90 Wilton Middlesbrough
Cleveland TS6 8JE England

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Eston Grange (0642) 43 (Ext No) Direct Line
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CHEMICALS
& POLYMERS
G R O U P

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

Your ref	Our ref	Tel ext	Date
	RTB/AB/MLM/753	2488	14 April 1987

(Received 27 April 1987)

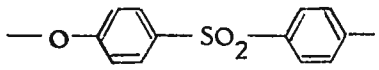
Dear Professor Shapiro

VERY LONG RANGE CHEMICAL SHIFT EFFECTS IN AROMATIC POLYMERS

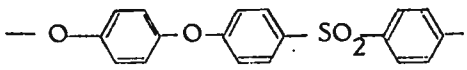
Since our last letter to you our Department has taken delivery of two spectrometers: a JEOL GX400 spectrometer primarily for solution state NMR applications and a Bruker MSL200 solids instrument. In addition we have recruited 3 new staff members including Nigel Clayden from Dr Dobson's Oxford University group and Geoff Nesbitt from Professor Robin Harris' group at Durham. Both installations have progressed fairly well to-date, so we are keeping our fingers crossed!

Much of my work over the last year or so has involved determination of the molecular structures of poly arylene ether sulphones, ketones and copolymers. As well as end group analysis several copolymers have been sequenced and it is observations from this work that I would like to report.

A sulphone copolymer composed of units I & II is prepared from condensation of 44' dichlorodiphenyl sulphone and a mixture of potassium salts of hydroquinone and 44' dihydroxydiphenyl sulphone. Transetherification, or ether scrambling (1), was believed to occur in this polymerisation.

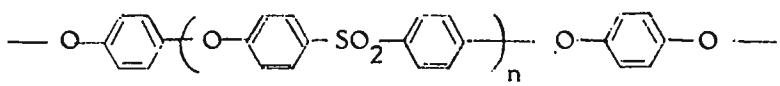


I



II

In the absence of transetherification sequences are produced:



where n has odd value integers ie 1, 3, 5 etc. In the presence of transetherification even values of n can be produced. Thus to investigate transetherification it was necessary to identify a resonance unique to the sequence above where n = 2.

A typical spectrum taken at 67.9 MHz in d_6-dmso at 80°C is shown in figure 1a, the most informative reasonances were those arising from the carbons 'a' and 'b' in the unit

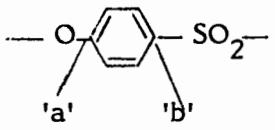
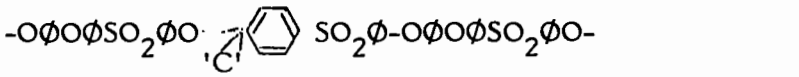


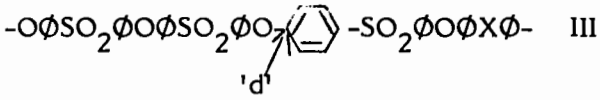
Figure 1b shows an expansion of the resonances of type 'a' carbons. The assignments of these resonances labelled A-F in 1b in relation to n values are:

A	⩾ 2
B	1
C	⩾ 3
D	⩾ 3
E	2
F	⩾ 3

Some interesting chemical shift differences are observed, for instance in the sequence



the resonance from carbon 'c' is incremented by -0.04 ppm when the extreme left-hand side ether group is replaced by a $-SO_2-$ group. This effect is 'seeing' an effect which is 3 benzene rings along the chain. Similarly we have found that replacing an ether by sulphone in III at position X changes the chemical shift by 0.12 ppm carbon type 'd'



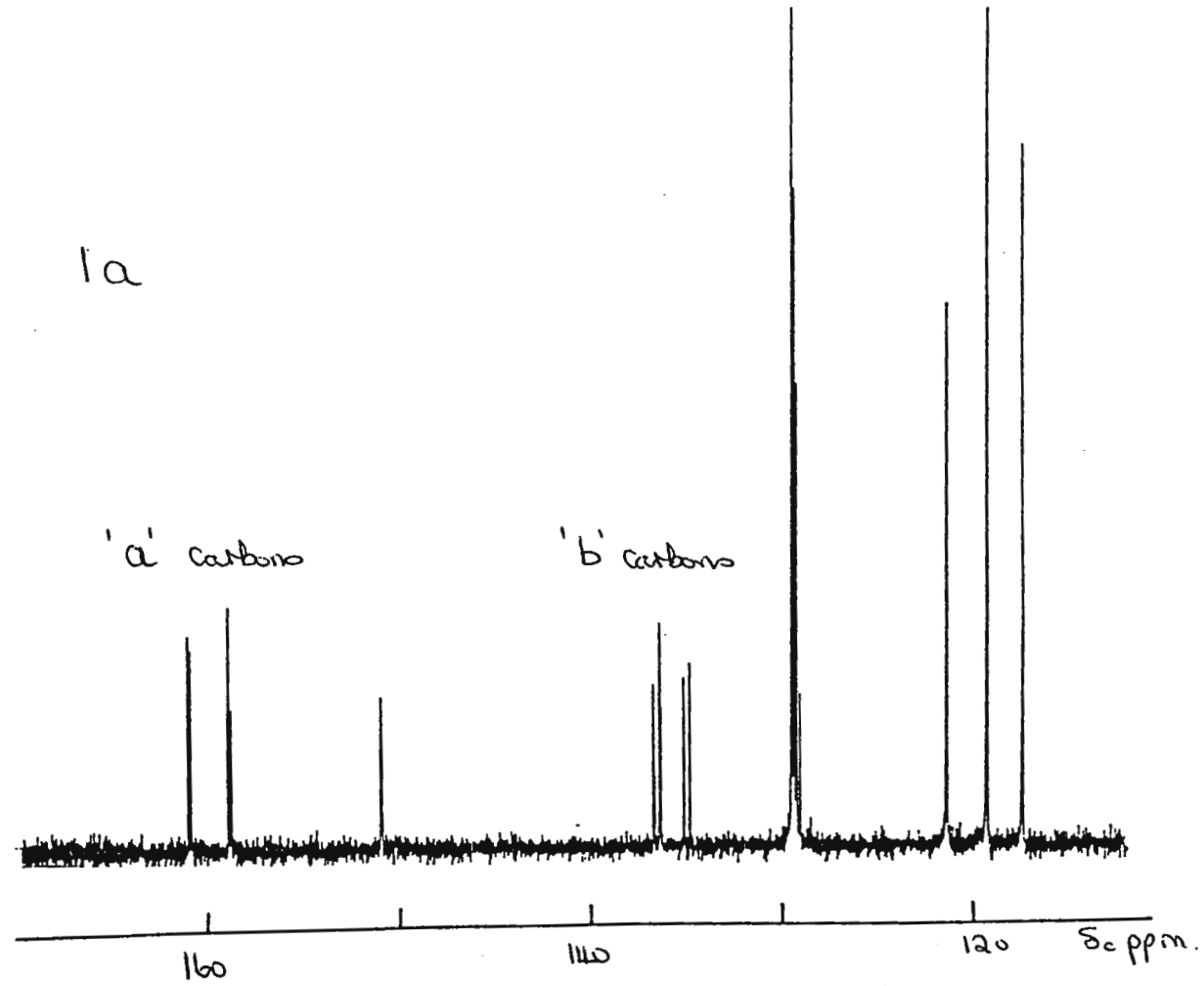
III

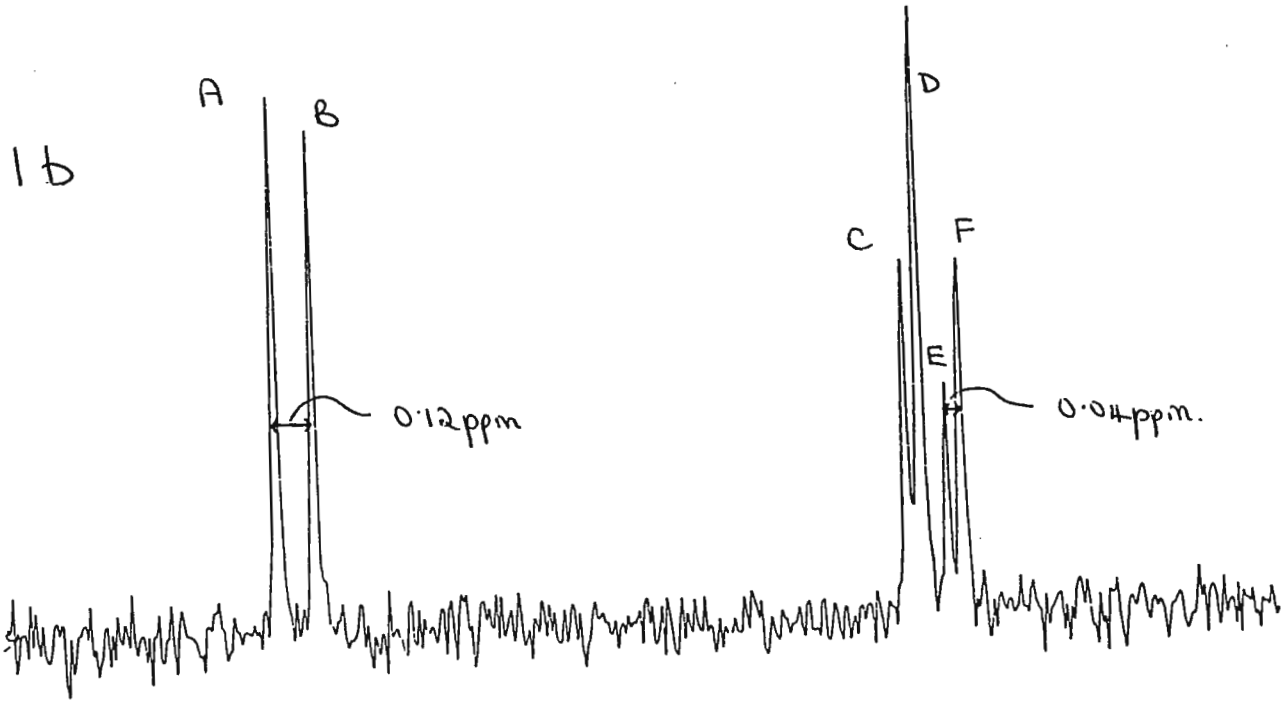
A detailed report of this work and two other aryl ether sulphone copolymers has been submitted to British Polymer Journal.

Sincerely

A BUNN
Analytical & Polymer Science Group

Ref 1 - Attwood T E, Newton A D & Rose J B, Br Polm J, 1972,4,391


1a
'a' carbons
'b' carbons
160
140
120
δc ppm.


1b
A
B
D
C
F
E
0.12ppm
0.04ppm.

Montana State University
Bozeman, Montana 59717

Department of Chemistry
College of Letters and Science

Telephone (406) 994-4801

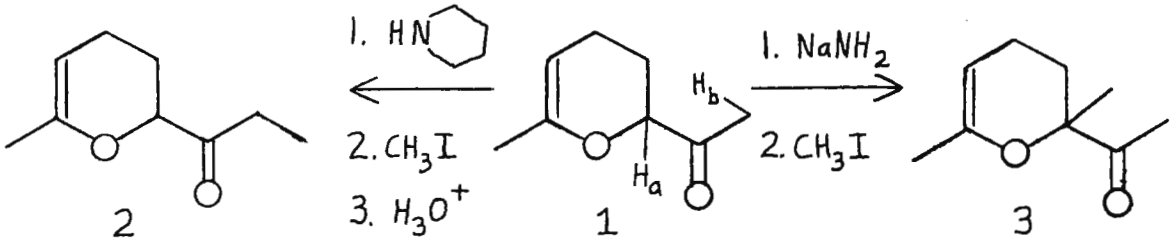
April 23, 1987
(Received 29 April 1987)

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

Dear Professor Shapiro:

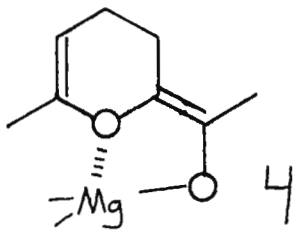
A Variable Temperature ^1H NMR Study of a $MgBr_2$ Complex with Methylvinyl Ketone Dimer

We are developing new methodologies for regioselective and stereoselective functionalization of methylvinyl ketone dimer (MVK-D). Enamine alkylation affords an efficient route to compound **2**, however, attempts to reverse the regioselectivity to obtain compound **3** (Rec. Trav. Chim. Pays-Bas, **98**, (1979)) have proven to be somewhat troublesome. Moderate amounts of regioisomer and dimethylated by-products often contaminate the desired product.



In addition to regioselective alkylations we are interested in controlling the stereochemistry of nucleophilic attack on the carbonyl by chelation control. Indeed, previous reduction attempts with metal hydrides and alkyl Grignard reagents have resulted in modest stereochemical control, i.e. preferential formation of erythro vs. threo alcohol (J. Org. Chem., 38, 627 (1973)).

To improve the yield of 3 and likewise the facial selectivity of nucleophilic attack to the carbonyl, we initiated a short range study of the complexation between MVK-D and a number of common Lewis acids. Three objectives we sought to achieve by complexing both oxygens of MVK-D were to a) weaken the bond between carbon and H_a, b) enhance the stability of the desired enolate which forms following abstraction of H_a (4) and, (c) facilitate facial differentiation of the carbonyl through 'Chelation Control' (JACS 1986, 108, 3847).



The paucity of available ^1H NMR data in the literature for Lewis acid complexes of alkoxy-substituted carbonyl compounds (JACS (1986), 108, 3847) prompts us to report preliminary data for the variable temperature solution spectra (in $CDCl_3$) for the intermediate formed between $MgBr_2$ and MVK-dimer.

The data clearly indicate a 1:1 complex is formed as the resonance for H_a is shifted from 4.25ppm for uncomplexed substrate (Figure 1) to about 4.8ppm for the complex at -50°C (Figure 4). Likewise the methyl ketone signal shifts from 2.25ppm (Figure 1) to about 2.5ppm (Figure 4). Unfortunately, for the purpose of Chelation Control, the system appears to lack conformational rigidity throughout temperatures studied as coupling patterns for H_a and the ring protons (1.9 to 2.1 ppm in uncomplexed MVK-D) are temperature dependent. The resonances at ca. 1.25ppm and 3.55ppm in the $MgBr_2 \cdot Et_2O$ complex (Figures 2-4) are due to Et_2O and may represent averaging between free and bound Et_2O. A variable temperature control study revealed little or no temperature dependence for chemical shifts and ^1H coupling patterns for uncomplexed MVK-D.

Follow-up research into the feasibility of this complexation, i.e. enhanced acidity of H_a vs H_b and chelation control are currently in progress.

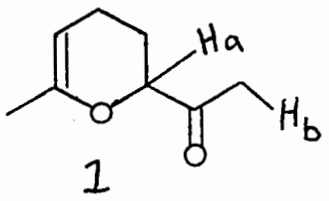
Sincerely,

Richard R Copp Jr.

Richard Copp
Research Associate

Bradford P. Mundy

Bradford P. Mundy
Professor of Chemistry



1

$1 \cdot MgBr_2$, -50°C

Figure 4

$1 \cdot MgBr_2$, -30°C

Figure 3

MVK-D · $MgBr_2 \cdot O(CH_2CH_3)_2$

$1 \cdot MgBr_2$, -10°C

Figure 2

Ha

Hb

1, 23°C

Figure 1

5 4 3 2 1 ppm

345-26

University of Strathclyde

Department of Pure and Applied Chemistry

Thomas Graham Building,
295 Cathedral Street, Glasgow G1 1XL Tel: 041-552 4400

PB/MAS

23rd April, 1987 (Received 1 May 1987)

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

Dear Barry,

Prevention of Condensation on the Base of a Superconducting Magnet

The problems associated with the water condensed from the atmosphere accumulating on the base flange of a superconducting magnet, and causing corrosion are well known. We have come upon a remedy in the form of a powerful water absorbent "WINDOWIZ". This was developed by colleagues here and is sold by:

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Originally made to mop up water condensing on the inside of windows in the Scottish Winter (climatic conditions which I'm sure never occur in the lands of Dallas and Dynasty), this comes in the form of knitted cloth tubes containing the absorbent polymer, which is wound round the magnet on the top of the flange.

Although the makers say the absorbent can be regenerated by hanging in a warm place, this is not really necessary as regeneration occurs spontaneously when the humidity of the room drops. The device serves to absorb the water which forms when the ice block on the magnet melts with (e.g.) sudden increase in the room heating. A 72 inch length of WINDOWIZ will just encircle our WM 250 magnet, at a few pounds. The manufacturers will make other lengths to order.

Regards and best wishes,

Peter Bladon.

Peter Bladon

The NMR evolution continues:

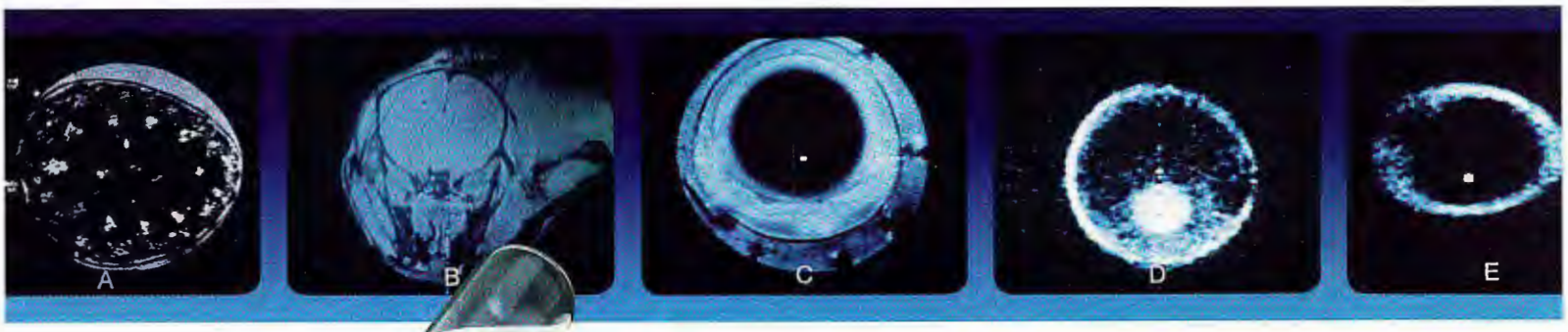

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Fig. C: A cross sectional image of a mouse eye, 3 mm in diameter. Resolution 20μ x 20μ x 250μ.
Fig. D: Image of an ovum from laevis (frog egg). Resolution 10μ x 10μ x 250μ.
Fig. E: Diffusion of water through a piece of nylon. Resolution 50μ x 50μ x 1000μ.

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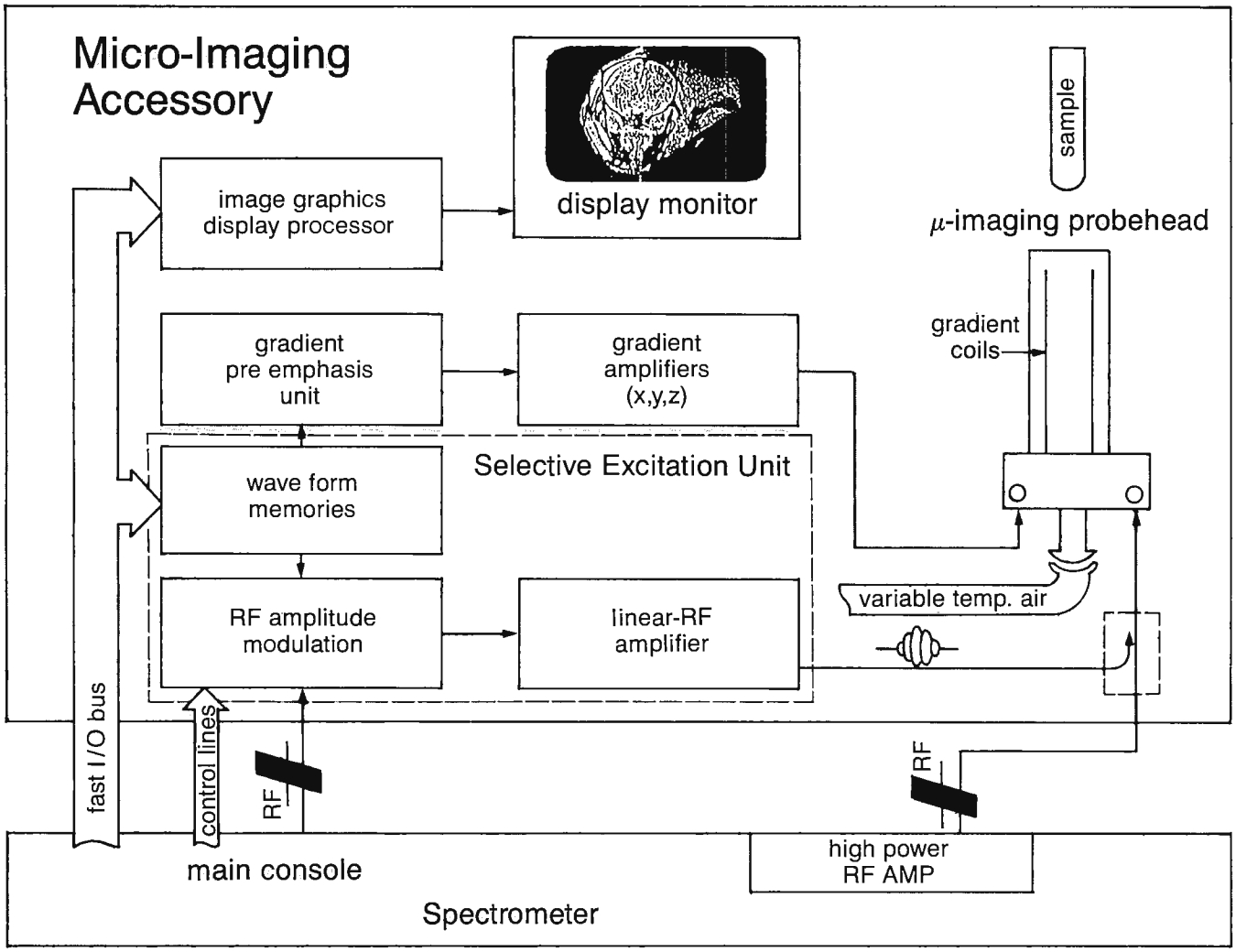
*Other nuclei available upon request



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DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service
National Institutes of Health
Bldg. 2, Room B2-02

National Institute of Diabetes and
Digestive and Kidney Diseases
Bethesda, Maryland 20892

April 29, 1987
(Received 4 May 1987)

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

Shaped Pulses on the Rise

Dear Barry:

With the popularity of shaped pulses on the rise, there is a need for an inexpensive, off the shelf RF modulator. Ideally, the device should be:

1. broad band
2. bipolar
3. linear

A balanced mixer or related device fills requirements 1 and 2 but has a nonlinear transfer function. When driven by a current source, things improve, and with a square component of the drive function added in, the device becomes a reasonable linear modulator. Figure 1 shows the schematic of such a circuit, using a Mini Circuits PAS series attenuator. The circuit will operate for functions of $\geq$ 1 ms duration when driven from a voltage source. When driven by a DAC, the squarer can be deleted and the correction done by software.

Fig. 2 shows the result of the circuit when driven by a 1 kHz triwave:

Input triwave ±10 V. Output RF:650 mVpp (100 mV/div), 100 Mhz.
Insertion loss ~9 db, Input level $\leq$ 10 dbm

Please credit this contribution to Dennis Torchia.

Sincerely,

Rolf Tschudin
Laboratory of Chemical Physics

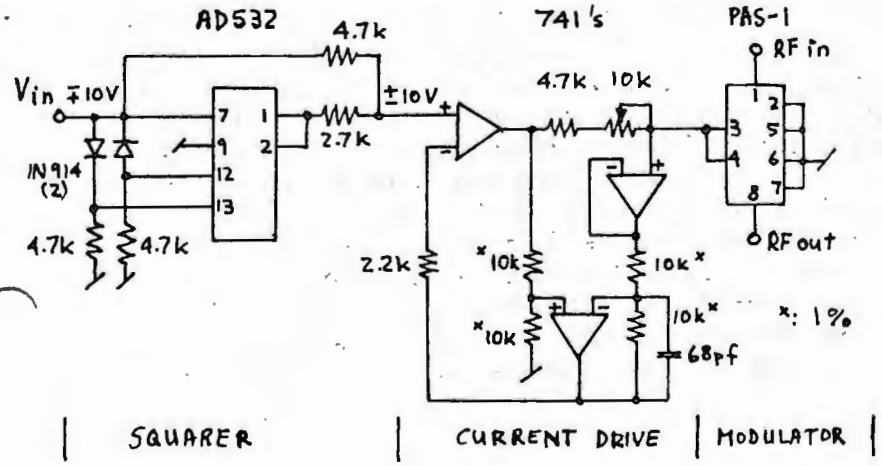


FIG. 1. RF MODULATOR

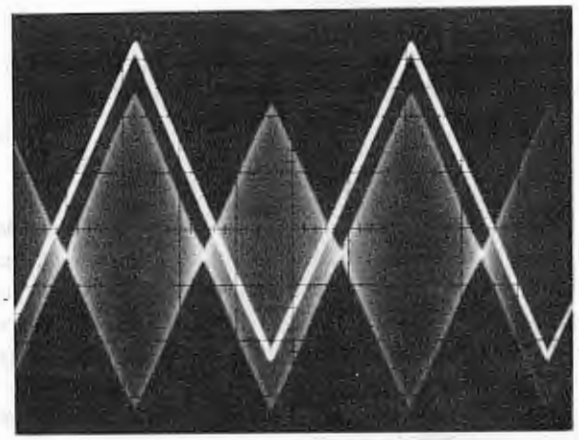


FIG. 2

Lehigh University

Department of Chemistry
telephone (215) 758-3470

Seeley G. Mudd Building 6
Bethlehem, Pennsylvania 18015

(Received 11 May 1987)

May 5, 1987

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

Aliphatic Material in
Dopa-Melanin

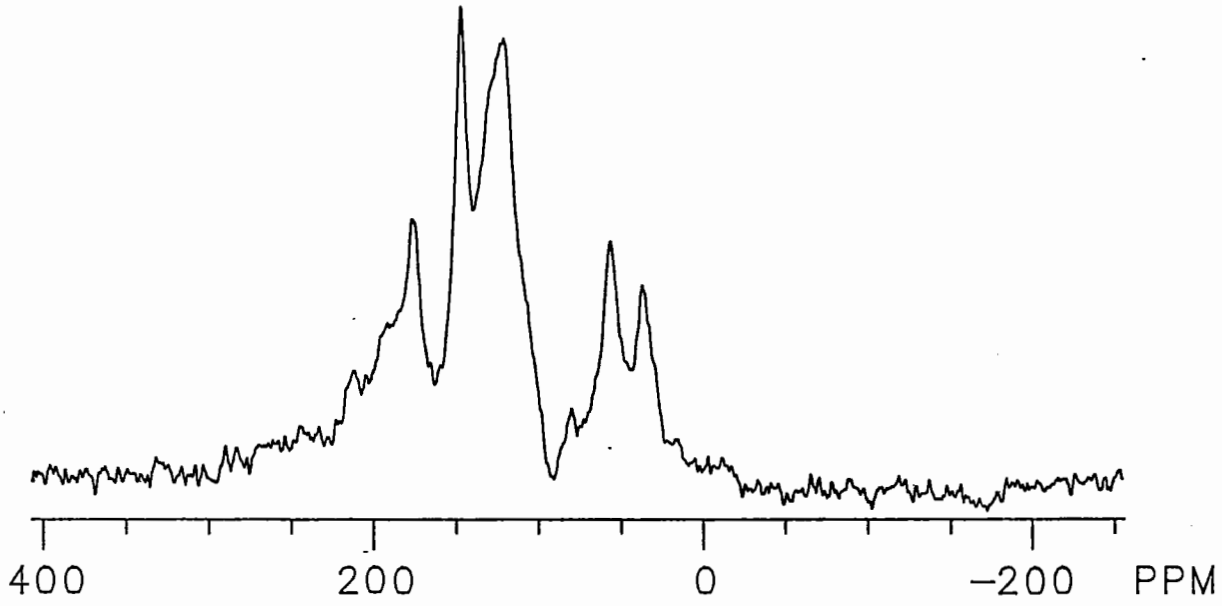
Dear Professor Shapiro,

The NMR groups at Lehigh University are pleased to make our first contribution to the TAMU newsletter. Our current facilities include a JEOL FX 90 Q solution instrument and a General Electric NMR Instruments GN-300 with home built solids equipment. In a unique arrangement, Air Products and Chemicals, Inc. and Lehigh University are jointly acquiring a Bruker AM-500 unit for solution studies. This instrument is currently being installed. Each institution will have access to the 500, although it is located in the NMR lab at Lehigh. A project jointly directed by Drs. Foster and Roberts is an inquiry into the structure of the biological pigment melanin utilizing solid-state NMR; our preliminary results are the subject of this report.

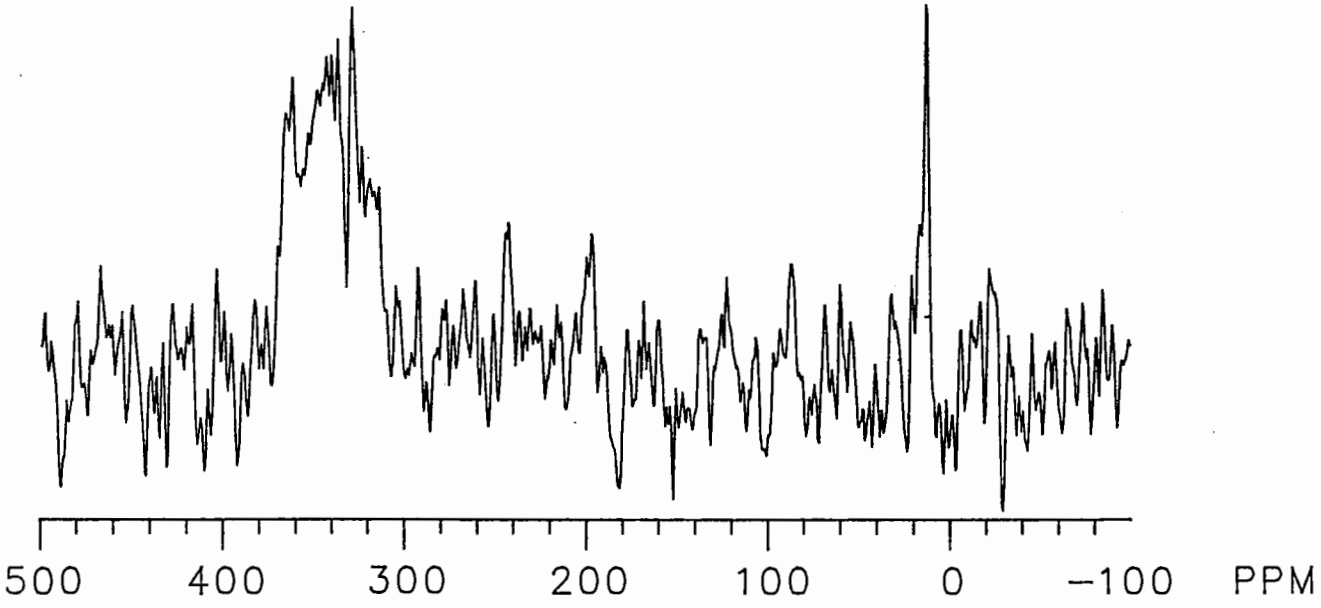
Eumelanins are animal pigments present in the skin, hair and eyes that consist of heterogeneous polymers with extensive cross-links formed from tyrosine by the enzyme tyrosinase in melanocytes. Although the precise chemical structure of any melanin is unknown, there appears to be agreement that indole, hydroxyindole, indole-quinone and pyrrole units are present in the polymer. Synthetic analogs of melanins have been prepared enzymatically from tyrosine and autoxidatively from dihydroxyphenylalanine (dopa) or 5,6-dihydroxyindole, since these compounds are proposed intermediates in the formation of melanin. An arguable issue concerning the structure of natural and synthetic melanins involves the presence of uncyclized material in the polymer (Swan and Waggott (1970) J. Chem. Soc. (C), 2409; and Hearing et. al. (1980) Biochim. Biophys. Acta, 611, 251.). The insolubility of the melanin pigment has limited the information obtainable by liquid-state NMR. However, our preliminary studies with solid-state NMR indicate the presence of aliphatic groups in dopa-melanin.

Dopa-melanin was prepared by autoxidation of L-dopa with air at pH 10 and dried under vacuum at 60 $^{\circ}$ C. The natural abundance ^{13}C and ^{15}N NMR spectra of this melanin were obtained with standard cross polarization/magic angle sample spinning techniques. The results shown below indicate the presence of aliphatic carbons and primary amines, which would be expected if some of the starting material had not cyclized or if some unpolymerized monomer units were entrained within the macrostructure. The aromatic portion of the polymer yields very broad spectral features, representative of their heterogeneity. To our knowledge, such results have not been convincingly demonstrated by any other method. Further investigations are in progress to determine the nature of the aliphatic material.

CARBON—13



NITROGEN—15



G. Andrew Duff
Andrew Duff
Graduate Student

William Anderson
William Anderson
Director of Instrumentation

Natalie Foster
Natalie Foster
Assistant Professor

James E. Roberts
James Roberts
Assistant Professor

PHILIP MORRIS

U.S.A.

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

May 8, 1987
(Received 15 May 1987)

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

Monitoring Biosynthesis of Wheat Cell Phenylpropanoids *in Situ*

Dear Barry:

Lignins and suberins are complex plant cell wall macromolecules comprised very largely of phenylpropanoid residues derived from l-phenylalanine and considered to be covalently linked to carbohydrates and to lipids, respectively. The bonding pattern of these important structural materials within cell walls has never been established. By feeding specifically labelled ^{13}C-ferulic acid over extended durations to seedlings of *Triticum aestivum*, and using ^{13}C CP/MAS NMR, we have been able to identify the major resonances due to specific carbons in the propanoid side chains of these cell wall polymers *in situ*. The signals were found to differ significantly from those of synthetic lignins, long considered to approximate natural lignin structure.

Figure 1 shows the spectra of wheat roots from seedlings fed either [2-^{13}C] ferulic acid or natural abundance (^{13}C) ferulic acid. The difference spectrum reveals ^{13}C enrichments at 114.6, 74.1 and 39.7 ppm. The signal at 114.6 ppm can be assigned to C-2 of ferulic acid in free or bound form. The 74.1 and 39.7 signals correspond to methine and methylene carbons that originated from the ferulic acid. Synthetic lignin prepared by the dehydrogenative polymerization of monolignols exhibits signals at 83-84 and 53-54 ppm while the signals corresponding to those observed in *T. aestivum* are essentially absent. This result emphasizes the importance of studying lignin structure in the intact plant tissue.

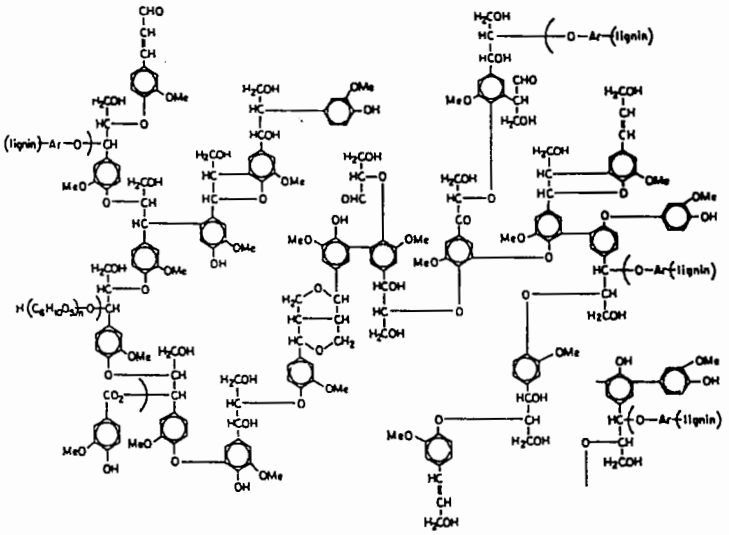
This work is a collaboration with Dr. Norman Lewis of Virginia Tech.

Sincerely,

Jan Wooten

J. B. Wooten, Ph.D.
Research Scientist

Attachment



A schematic constitution of spruce lignin.

FIGURE 1. (A) ^{13}C CP/MAS Spectrum of T. aestivum roots administered [2-^{13}C] Ferulic acid. (B) Control (C) Difference

Georgia State University
a unit of the university system of georgia

university plaza
atlanta, georgia 30303

Department of Chemistry
April 24, 1987
(Received 4 May 1987)

Interfacing a Varian VXR-400 and an IBM PC.

Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77483

Dear Professor Shapiro:

The Varian VXR NMR spectrometer can transfer data to an IBM PC through the serial printer output port. The VXR printer configuration must be set to the IDS460 mode. The IBM PC should be set up to receive the data by writing a BASIC program which transfers the data to a disk file (below).

Most BASIC programming languages allow the programmer to set the PC buffer size. It is advisable to set the buffer size to the maximum for the PC. For the cable we have used a "straight through" cable, RS232 connectors, with lines 2 and 3 crossed.

The LPRINT command will send the current FID or spectrum (after a WFT command). Phased data are found only in DSKØ.PHASFL. To transfer data first begin the BASIC program on the PC. It will wait for the 'return' after LPRINT (DSKØ.PHASFL,NI,NF) (NI = starting sector, NF = ending sector) on the Varian. After the data has been transferred, hold down the control key, and hit the break key on the PC. Type 'SYSTEM' to close file. The first 8 lines of the transferred file contain information about the Varian disk files. The rest of the lines have data in double columns of E format data:

$data_i$ $data_{i+1}$

$data_{i+2}$ $data_{i+3}$

Positive values are given as n.nnnnnnE nn. Most programs (LOTUS for viewing data, FORTRAN for calculations), will not allow the space before the E; this can be removed with the DOS program EDLIN.

Although data transfer is time consuming (10 sectors take 3-4 minutes) the ability to transfer data to the PC is very useful for some calculations and for sites which do not yet have a Varian-mainframe connection. We thank Peter Rinaldi of Varian for useful discussions.

Sincerely yours,

Dabney White Dixon Xiaole C. Hong Scott E. Woehler

(continued on page 37)

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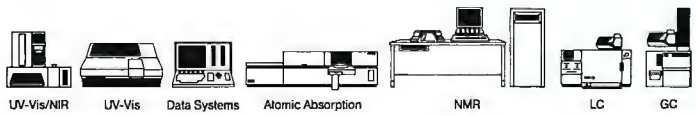

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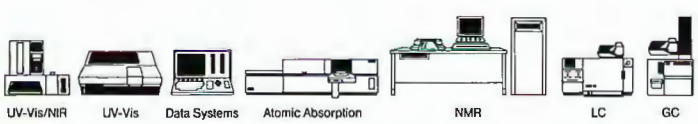

INTELLIGENT SOLUTIONS FOR YOU

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(continued from page 34)

```
1 OPEN"COM1:9600,N,7,1,RS,CS,DS,CD" FOR INPUT AS #1
2 OPEN"b:nmr1.prn" FOR OUTPUT AS #2
3 FOR I=1 TO 1000
4 FOR J=1 TO 1024
5 B$=INPUT$(1,#1)
7 PRINT#2,B$;
8 NEXT J
9 PRINT I;
10 NEXT I
Ok
```

Comments on various lines:

1: 9600 baud, no parity, 7 data bits, 1 stop bit

2: extension .PRN allows the file to be imported to LOTUS 123 for plotting

3: I loop prints (on the PC) the number of transferred characters in units of 1024 characters

4: J loop reads characters one at a time

UNIVERSITY OF SOUTH CAROLINA
COLUMBIA, S. C. 29208

SOUTH CAROLINA MAGNETIC
RESONANCE LABORATORY

(803) 777-7341

(Received 30 April 1987)

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

Re: Some Comments on Liquid State ^{95}Mo NMR

Dear Barry:

During this past year I have had the pleasure of working with Professor Shelton Bank of SUNY Albany. Shelly has been on sabbatical leave with me this year. One of the problems we have been working on involves the utilization of liquid and solid state ^{95}Mo NMR as a means for the characterization of surface adsorbed Molybdenum species. With this goal in mind we have been looking at some "simple" Molybdenum clusters. In many instances one observes fewer resonances than there are unique Molybdenum atoms in the cluster. The typical argument to rationalize this paucity of peaks is to claim either chemical dynamics or excessive line broadening of the ^{95}Mo resonance due to quadrupole relaxation. We have used the temperature dependence of this disappearing act to, in some cases, observe the missing lines. However, this strategy is not a general one.

Two compounds $[Bu_4]_4[Mo_8O_{26}]$ and $[Bu_4]_4[Mo_4O_{10}(OCH_3)(NNPh_2)_2]$, I and II respectively, each with tetrahedral and octahedral molybdenum atoms give rise to a single peak in the room temperature ^{95}Mo NMR. For compound I the crystal structure reveals octahedral and tetrahedral molybdenum atoms in the ratio of 3:1. The spectrum at 292 degrees has one sharp line at 18.4 ppm, with respect to Na_2MoO_4, in CD_3CN. Heating the sample to 337 degrees brings about the sharpening of the signal and a small change in chemical shift to 22 ppm. Significantly, a broad peak at -8 ppm is clearly evident with the expected intensity ratio of 3:1. Most importantly, the process is reversible.

Unfortunately, the strategy is limited by the stability of the cluster. For compound II the crystal structure shows octahedral and tetrahedral molybdenum atoms in the ratio of 1:1 yet the ^{95}Mo NMR has a single resonance at 24.6 ppm at 292 degrees. Heating the sample to 337 degrees leads to a spectrum with signals at -68, -48, -20 and 38 ppm. Most importantly when the sample temperature is lowered back to 292 degrees there is no signal at 24.6 ppm and there are resonances at -68, -48, and -20 ppm. Clearly, there has been some chemical transformations and

(continued on page 40)

(continued from page 38)

the desire to observe the "missing" resonance is thwarted.

It appears that for compound I the origin of the peak larceny is due to the quadrupole relaxation. For compound II the quadrupole is the probable source, but chemistry prevents a detailed analysis. We are continuing our work on these compounds in the solid state with and without high speed magic angle spinning. We will report our results on these experiments at a later time.

Sincerely,

Paul D. Ellis

Shelton Bank

The Complex Carbohydrate Research Center at the University of Georgia is seeking an

NMR technician

to begin June 1, 1987, or as soon as possible thereafter.
The successful candidate will operate state-of-the art NMR equipment, including Bruker AM-500 and AM-250 (narrow bore) spectrometers with Aspect-3000 (process controller) data system, both connected to an autonomous data station. The technician will collaborate with the Center's NMR spectroscopist, carbohydrate researchers, and instrumentation manager. B.S. or M.S. in chemistry, basic understanding of pulse-FT NMR required. Experience in operating NMR instrumentation and/or in interpretation of NMR data would be an advantage. Salary range in the upper teens, depending on experience.
Interested candidates should address inquiries or letter of application (including curriculum vitae) and two letters of reference to:

Dr Herman van Halbeek, Complex Carbohydrate Research Center.
University of Georgia, P.O. Box 5677, Athens, Georgia 30613,
404-546-3312.

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Thanks for bringing this job advertisement to the notice of your readers.
Sincerely yours,

Herman van Halbeek
Assistant Professor of Biochemistry
and Chemistry

Postal Address: Russell Laboratories, P.O. Box 5677, Athens, Georgia 30613 USA
Office Telephone: 404-546-3312 Bitnet: UGA PALBERSH

University of Alberta
Edmonton

Department of Biochemistry

Canada T6G 2H7

474 Medical Sciences Building, Telephone (403) 432-5460

April 28th, 1987
(Received 4 May 1987)

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

Dear Barry:

Title: New VXR-500 & Tape Backup for NT-300

Since I'm normally prompt in sending in my 'subscription' contribution, the lab was quite interested in the often mentioned pink ultimatum stage that arrived this time. The major happening that has occurred in the laboratory these past months has been the installation of a Varian VXR-500 NMR spectrometer. This is certainly one beautiful system which works very well. We just ran this last week, for example, a 2QF-COSY of a protein of MW ~12,000 at 1 mM and got beautiful results.

On another subject, a common problem is data storage. With more and more 'routine' use of 2D NMR, and ever increasing 2D data matrices [2K x 2K → 4K x 4K → 8K x 8K, etc.], one can certainly accumulate enormous amounts of data what has to be stored for processing later. Our older NT-300 WB is particularly bad for data storage since it is equipped with the CDC Hawk disc drives with limited storage capacity on expensive disk cartridges. We have decided that a fast, convenient and economical storage method is streaming magnetic tape, and have interfaced (hardware & software), an Advanced Digital Information Corporation streaming tape drive to our Nicolet 1280 computer. This gives us 57.5 Megabytes of user data storage per tape, with storage and retreival of individual files possible. The way we have programmed it with handshaking and error checking it is not super fast [ex. backup of NMC program (139 sectors) takes 26 seconds] but is convenient, reliable and one can back up as many as 9 disk cartridges/tape.

More details are available on request.

Best regards,

Gerry McQuaid Robert Boyko Brian Sykes

BDS/ss

FOX CHASE
CANCER CENTER
AMERICAN ONCOLOGIC HOSPITAL ■ CENTRAL & SHELMIRE AVENUES ■ PHILADELPHIA, PENNSYLVANIA 19111

TRUMAN R. BROWN, Ph.D.
Director, Nuclear Magnetic Resonance
and Medical Spectroscopy
215/728-3049

May 19, 1987
(Received 25 May 1987)

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

Re: Automatic quantification of low S:N spectra

Dear Dr. Shaprio:

In the analysis of spectra obtained from biological samples, the existence of a variable background and the relatively low S:N ratio of some peaks may make quantification by traditional methods unreliable. We have recently developed a technique for quantification of such spectra which automatically seperates slowly varying background, random noise and peak components. Thus we are able to determine estimates for peak positions, peak heights, the errors in peak height estimates, peak areas and the errors in peak area estimates. The technical details of this method and the calibration based upon analysis of simulated spectra will be reported in a future issue of the Journal of Magnetic Resonance. We describe here an application of the technique to the analysis of two ^{31}P spectra from a human calf. These spectra comprised either 1 or 128 scans, obtained using a Siemans's Magnetom operating at 1.5T (^{31}P = 25.6 MHz, dwell time 250 msec, pulse length 1 msec).

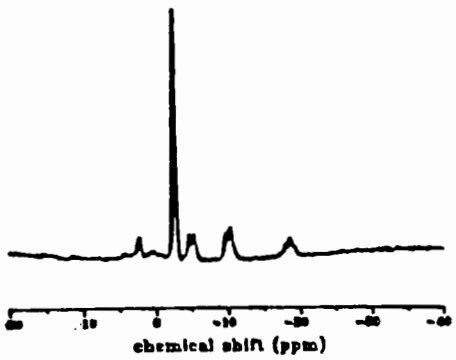
Figures 1a and 1b show the unsmoothed 128 and 1 scan data respectively and Figure 1c demonstrates the result of smoothing the 1 scan data using our technique. Although there is not as much detail as in the 128 scan spectrum, the shape of the background, the peak region positions and the relative peak shapes are similar for the 128 unsmoothed and 1 scan smoothed spectra. Visually therefore, our technique provides good agreement. More important is the accuracy of the quantification and this is shown in Table 1. In both cases the estimates are obtained automatically from the raw data using a computer program which implements our technique. We see that five different peak regions are identified in both cases. For three of these regions the estimates of maximum positions are identical for both spectra, for the other two regions, the differences are 0.1 and 0.3 ppm. The differences in peak maximum height estimates for the two spectra are all within the predicted errors due to the random noise. For peak regions 1,4, and 5, the area estimates for the two spectra are very close and for peak regions 2 and 3 they are still within three standard deviations of each other. That the estimates of peak areas might be biased on the low side for broader peak regions was predicted by the analysis of simulated spectra. In summary, we are very encouraged by the results obtained using this technique and will be using it to quantitate our low S:N spectra in future.

Sincerely,

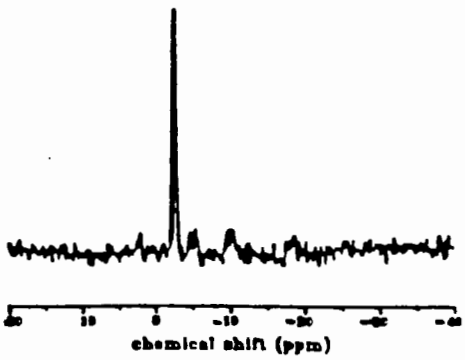
Sarah J. Nelson William J. Thoma Truman R. Brown

Figure 1

a. 128 scan spectrum



b. 1 scan spectrum unsmoothed



c. 1 scan spectrum smoothed

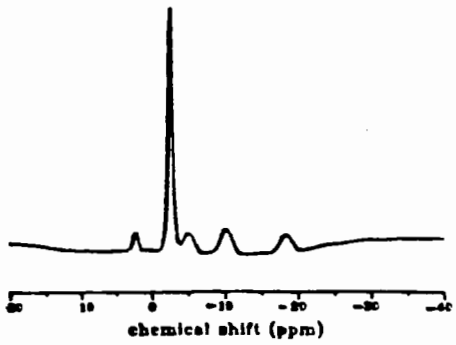


Table 1. Comparison of the quantitation obtained using either the 1 scan or 128 scan data.

PEAK REGION		MAXIMUM POSITION (ppm)	MAXIMUM HEIGHT value	sd	AREA value	sd
1	1 scan	-18.5	8.8	1.7	46	6
	128 scans	-18.5	8.0	0.1	42	1
2	1 scan	-9.9	8.8	1.7	60	7
	128 scans	-10.2	11.0	0.1	80	1
3	1 scan	-5.2	8.6	1.7	43	6
	128 scans	-5.2	8.4	0.1	60	1
4	1 scan	-2.5	84.6	1.7	244	7
	128 scans	-2.5	85.3	0.1	249	1
5	1 scan	2.3	6.7	1.7	20	4
	128 scans	2.4	6.6	0.1	19	1

DE GUIGNÉ
TECHNICAL CENTER
WESTERN RESEARCH

Stauffer Chemical Company
1200 S. 47th St. / Richmond, CA 94804 / Tel. (415) 231-1000 / TWX (910) 382-8174

May 20, 1987
(Received 25 May 1987)

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

Subject: "Rotational Isomers of a Thiocarbamate SS-dioxide"

Dear Barry:

We recently obtained a proton NMR spectrum of a thiocarbamate SS-dioxide (I) using a Varian XL-400 NMR spectrometer. The aliphatic portion of the spectrum is rather complex and is shown in Figure 1. At room temperature, thiocarbamates generally exhibit free rotation around the C-N bond. However, thiocarbamate SS-dioxides always show hindered rotation and exhibit two sets of resonances for the rotamers. The spectrum indicates that compound I has a rotamer ratio of 60:40. Due to the presence of an asymmetric carbon in compound I, the spectrum exhibits additional complication. Using the COSY and selective decoupling experiments, we have assigned the chemical shifts of the aliphatic protons of I. Based on diamagnetic anisotropy of the S-O bond, the major rotamer was assigned structure Ia and the minor rotamer Ib. The chemical shifts and coupling constants (in parenthesis) are listed in Table 1.

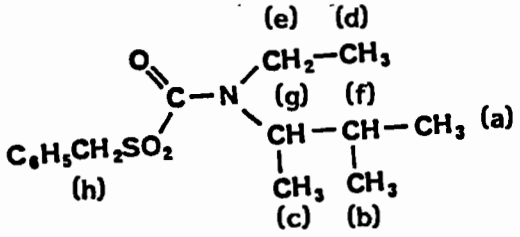
Sincerely yours,

C. K. Tseng

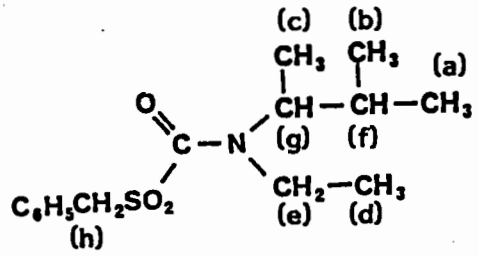
L. L. Chang

Table 1. Chemical Shifts and Coupling Constants of I

Rotamer	a	b	c	d	e	f	g	h
Ia	0.89 (6.5)	0.92 (6.6)	1.24 (6.7)	1.23 (7.0)	3.15;3.45 (13.6;7.0)	1.73	4.22 (9.6;6.7)	4.60
Ib	0.82 (7.0)	0.93 (6.6)	1.32 (6.8)	1.25 (7.1)	3.63;3.65 (15.7;7.1)	2.11	3.32 (9.9;6.8)	4.58



Ia



Ib

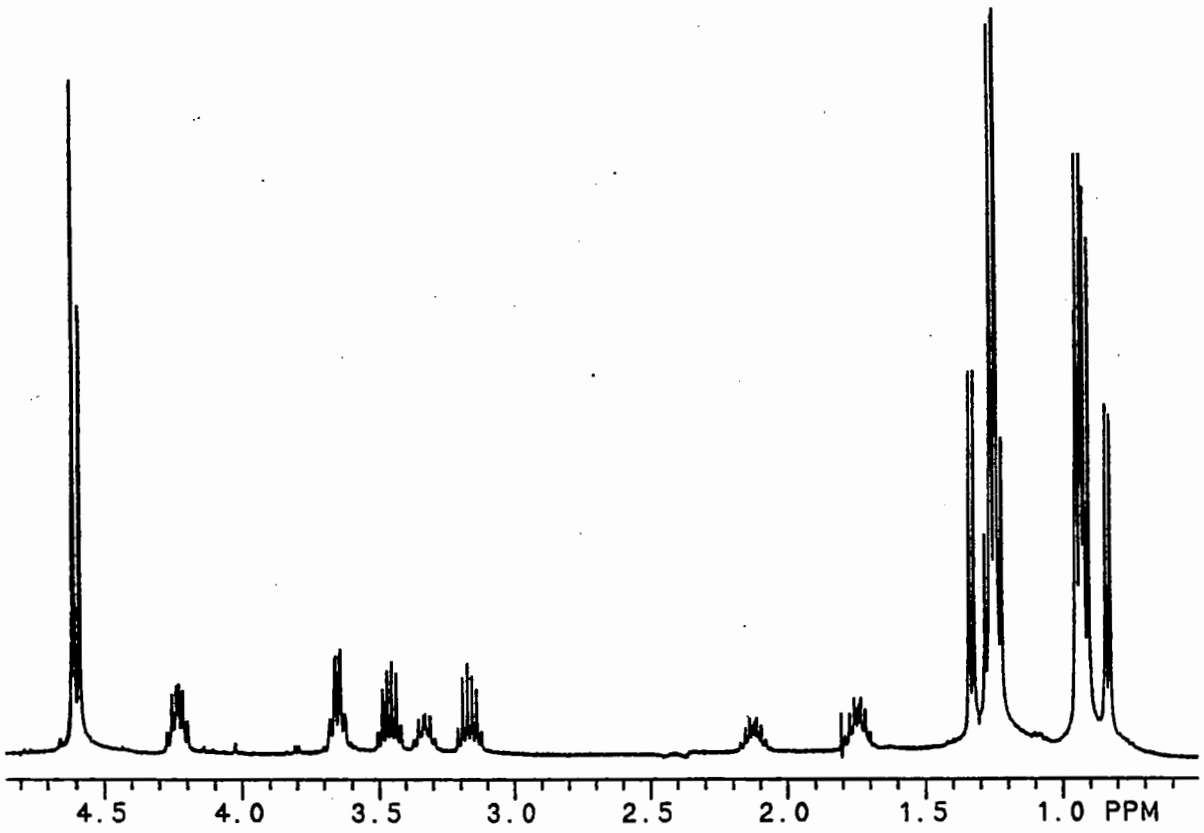


Figure 1. Partial Proton NMR Spectrum of I.

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DATE: May 14, 1987
OUR REF:
YOUR REF: (Received 18 May 1987)

Slice Selection for Localized Spectroscopy

Dear Professor Shapiro,

Localized spectroscopy is becoming an increasingly important tool for the in vivo study of metabolism. Several techniques have been proposed to obtain localization and the ones that make use of slice selection in three orthogonal dimensions show the most promise to yield quantitatively defined volumes.

In this contribution we want to illustrate the superior qualities of the hyperbolic secant pulse (1) for slice selection. Traditionally a sinc (sin(t)/t) modulated pulse has been used for slice selection in imaging experiments because of the sharp edges in its frequency spectrum. Thus, the spatial region from which the signal originates is sharply defined. In terms of retrieving all the signal from the selected slice, however, the sinc pulse is not 100 % effective. A typical example of a sinc pulse selected slice is given in figure 1a. Although a signal loss of, say, 10 % is not a serious problem in imaging, in localized spectroscopy three orthogonal slices have to be selected and the signal is reduced by 30 %.

The hyperbolic secant pulse can be used to invert the signal in a slice. Because ISIS (2) makes use of slice inversion to define the volume of interest this pulse can be applied in localized spectroscopy. The effective band in the frequency spectrum has sharp edges and yields virtually 100 % inversion within the slice (figure 1b). Moreover, it is, above a certain threshold, independent of RF power, making it perfectly suitable for use with a surface coil.

For in vivo spectroscopy, not only the sharp definition of the volume but also the most effective measurement of the magnetization in it is of importance. Consequently, the hyperbolic secant pulse should be preferred to the sinc pulse for slice selection in localized spectroscopy because of its superior sensitivity.

A. Connelly C. Counsell J.A.B. Lohman

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(2) R.J. Ordidge, A. Connelly and J.A.B. Lohman, J. Magn. Res., 66 (283) 1986.

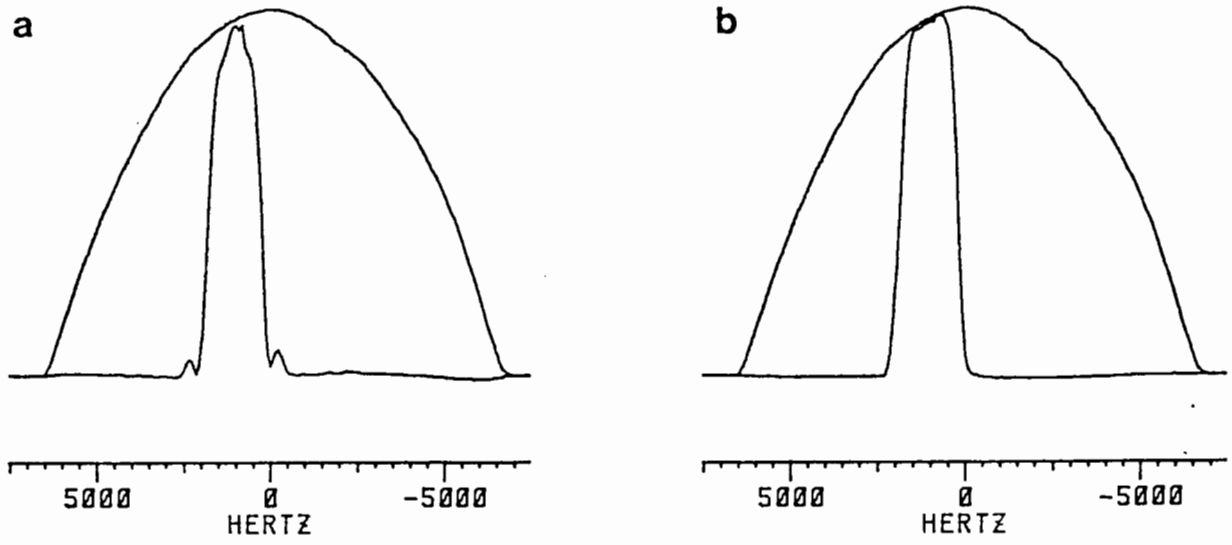

Figure 1

The top trace in each diagram is the unperturbed profile of a sphere in a magnetic field gradient. The bottom trace is the normalized profile of a slice as obtained with a one-dimensional ISIS experiment.
(a) Slice inversion using a sinc pulse. (b) Slice inversion using a hyperbolic secant pulse.

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Professor B.L. Shapiro
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Zürich, May 6, 1987
(Received 11 May 1987)

REMARKS ON E.COSY AND INTRODUCTION OF A NEW HIGH SENSITIVITY 2D CORRELATION EXPERIMENT CALLED SOFT-COSY

Dear Barry,

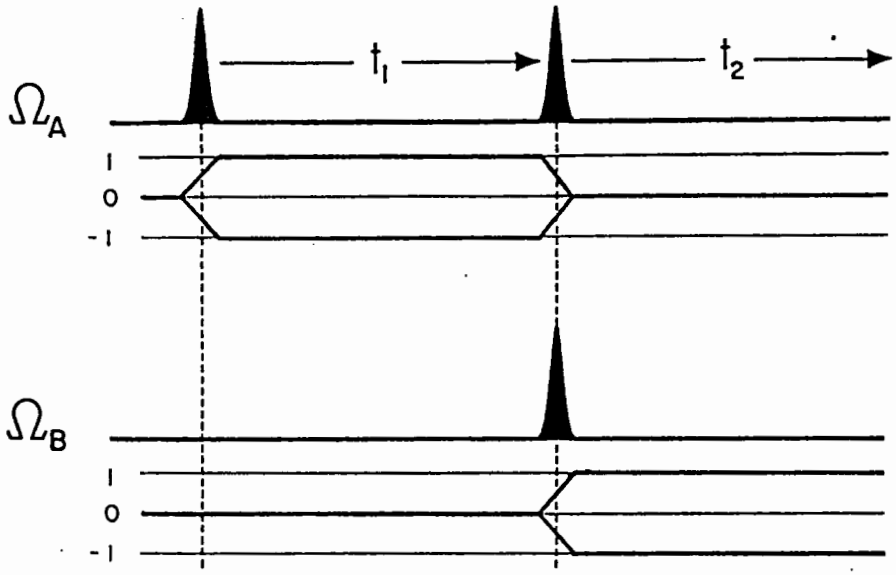
The purpose of this letter is twofold: (i) We want to respond to possible misconceptions about the E.COSY technique, and (ii) we like to report a frequency-selective 2D correlation technique called soft-COSY which also produces E.COSY cross peak multiplet patterns, however in some cases with considerably higher sensitivity.

Some spectroscopists might have gained the impression that E.COSY is a complicated technique requiring extensive linear combinations of different 2D data sets. Although E.COSY can be understood as a linear combination of independent multiple-quantum-filtered COSY spectra of different orders, this is not the way it should be realized in practice. The E.COSY pulse sequence is in fact identical to the one for multiple-quantum-filtered COSY, 90_{β}-t_1-90_{β} 90_{-x}-t_2 , differing only in the particular phase cycle for β. Here we give two convenient E.COSY phase cycles with 32 and 192 scans, respectively, the second leading to marginally better suppression of undesired multiplet components.

β	0^o	45^o	90^o	135^o	180^o	225^o	270^o	315^o
number of scans	10	-7	2	-1	2	-1	2	-7
	60	-41	12	-7	12	-7	12	-41

Negative signs indicate that the receiver reference phase is shifted by π for the respective scans. It is advantageous to perform the experiments in such an order that the receiver phase alternates between 0 and π. Further details can be found in a paper recently submitted to Journal of Magnetic Resonance.

Extraction of accurate J coupling constants from E.COSY spectra requires high resolution which in some cases might not be feasible for time or computer storage reasons. This led to the design of the "soft-COSY" technique which extracts restricted domains in 2D frequency space by soft, selective pulses, typically of Gaussian shape. The pulse sequence can be written:



If the pulses with frequencies Ω_A and Ω_B affect only the two active spins of a cross peak, E.COSY multiplet patterns are produced. Compared to E.COSY with one of the above phase cycles the sensitivity enhancement for example for a system of four mutually coupled spins is a factor 8. Further spins coupled to only one of the two active spins have no influence on the relative sensitivity.

An application of soft-COSY is shown in Fig.1a. It represents correlation between the protons $C_\delta H_2$ and $C_\gamma H_2$ in the proline[8] residue of the decapeptide antamanide. 256 t_1 experiments were recorded in 1.7 h using Gauss pulses of 30 msec duration (cut-off at 2% amplitude). The spectral width is in both dimensions 250 Hz. The sample contained 11 mg antamanide in 0.5 ml $CDC\ell_3$.

For comparison the same cross peak from a double-quantum-filtered COSY spectrum is shown in Fig.1b. It represents 19 h of instrument time. Many J coupling constants not accessible in the spectrum in Fig.1b can easily be extracted from the soft-COSY spectrum in Fig.1a. In cases where not too many cross peaks are of interest a number of soft-COSY experiments can turn out to be faster than a single non-selective E.COSY experiment because of the inherent sensitivity gain.

It should be noted that soft-COSY is by no means limited to the recording of individual cross peaks but might prove its virtues even better in recording spectral regions containing several cross peaks.

Yours sincerely,

R. Brüschweiler C. Griesinger Ö.W. Sørensen R.R. Ernst

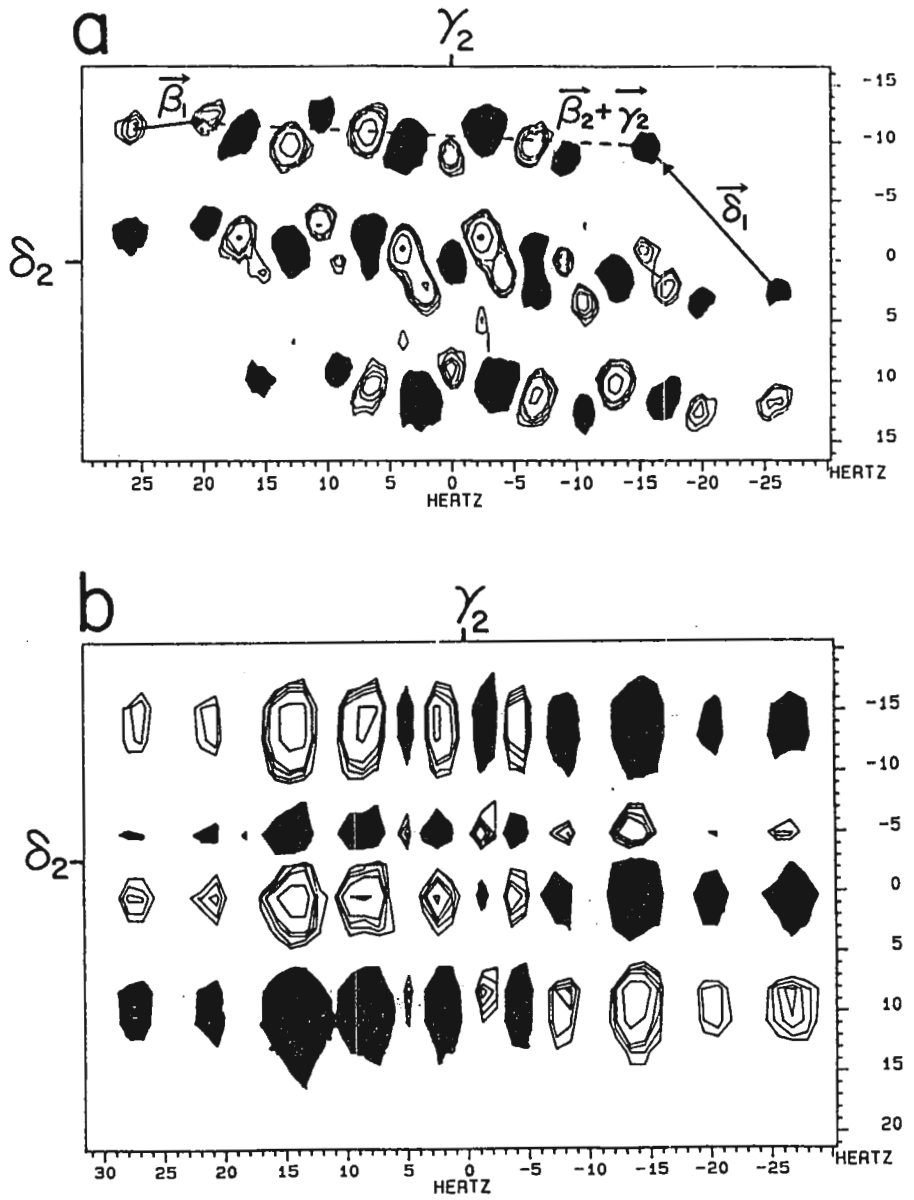


Figure 1

THE MILTON S. HERSHEY MEDICAL CENTER
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May 19, 1987
(Received 25 May 1987)

Department of Radiology
717 531-8044

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

Dear Dr. Shapiro:

Na^+ Transport Across Lipid Vesicle Membranes Studied by ^{23}Na Magnetization Transfer NMR

The Forsén-Hoffman magnetization transfer NMR techniques (1) are a powerful tool for studying slow chemical and conformational exchange processes. Applications of these techniques have mainly involved ^{1}H, ^{13}C and ^{31}P NMR spectroscopies. Recently, we have become interested in using ^{23}Na magnetization transfer NMR to study the kinetics of ionophore (e.g., monensin, gramicidin)-mediated transport of alkali ions across large unilamellar vesicle membranes. In principle, determination of the exchange transport rate constants from such studies is possible because (i) model vesicles with high internal ion concentrations can be readily prepared, (ii) the intra- and extravesicular cation resonances can be resolved on the chemical shift axis (Fig. 1) using an aqueous hyperfine shift reagent such as bis(tripolyphosphate)dysprosium(III); and (iii), linewidth measurements have suggested that the transport rate constants are within the range of those accessible to magnetization transfer NMR techniques. In practice, however, the matter is somewhat more complicated because magnetization transfer techniques require that one of the exchanging resonances be selectively saturated or inverted. In order to obtain a frequency selective pulse, a long "soft" pulse or a long-duration train of short "hard" pulses (DANTE) must be applied. However, for nuclei with a short spin-lattice relaxation time, relaxation during the application of the long selective pulse becomes important. As a result, the line can no longer be inverted or saturated.

In order to achieve selective inversion of either Na (in) or Na (out), we have used the "rotating frame" selective inversion scheme described by Robinson et al. (2). With the peak to be inverted on-resonance, the following sequence is applied:

$$90 - D1 - 90_{-\tau} - 90 - \text{acquire}$$

where the 90° pulses are non-selective "hard" pulses and D1 is equal to half the reciprocal of the shift difference between the internal and external resonances. Clearly, in order to achieve complete inversion, D1 must be much less than the spin-lattice relaxation of the nucleus of interest. We have met this condition for ^{23}Na by increasing the separation between Na (in) and Na (out) peaks through (a) the use of a high static magnetic field (9.4 T) and (b) by adjusting the mole ratio of Na^+ to shift reagent until a sufficiently large shift difference is obtained without excessive line broadening. Typical D1 values are 0.1 - 0.3 msec.

Figure 2a shows the selective inversion of Na (out) in the absence of exchange (no ionophore in the sample). After the injection of 5 μliters of a 50 mM methanol solution of monensin, exchange of Na (in) <==> Na (out) is induced. Selective inversion-recovery of Na (out) yields the spectra shown in Figure 2b. It is evident that monensin transports the inverted spins from the outside to the inside of the vesicles where the magnetization diminishes proportionately. Figure 3 shows the experimental and calculated curves. Since in this vesicle system exchange does not start until monensin has been injected into the sample, we are able to measure T_1 for Na (in) and Na (out) in the absence of transport. That the values of the kinetic parameters obtained from the inversion transfer experiments are reliable is supported by the fact that the experimental T_1's and those derived from the simultaneous curve-fitting of $M_z(\tau)$ vs τ for the two resonances are in excellent agreement. A complete study of the ionophore concentration-dependence and of the temperature-dependence of the exchange rates has been conducted. A manuscript with a full account of the findings is in preparation.

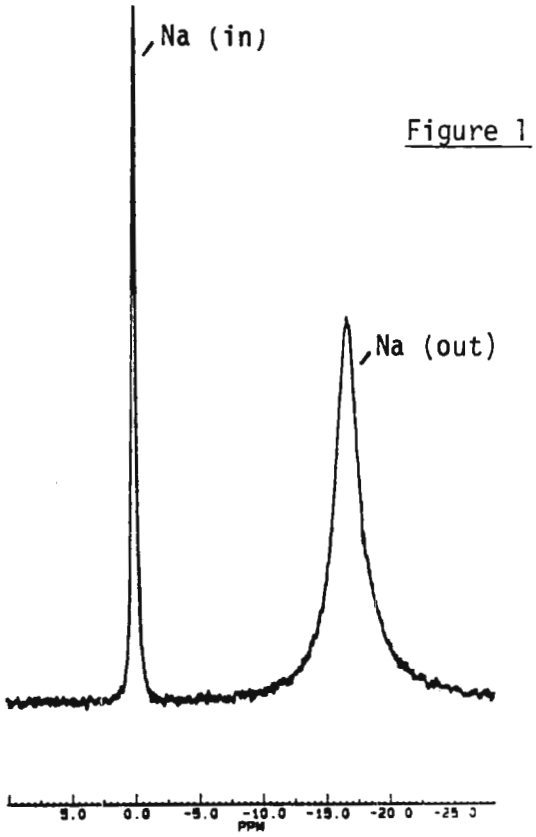

Figure 1

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2. Robinson, G., et al., J. Magn. Reson., 63, 314 (1985).

Sincerely,

Dikoma C. Shungu

Richard W. Briggs

NOTE: Please credit this communication to Dr. R. W. Briggs' account.

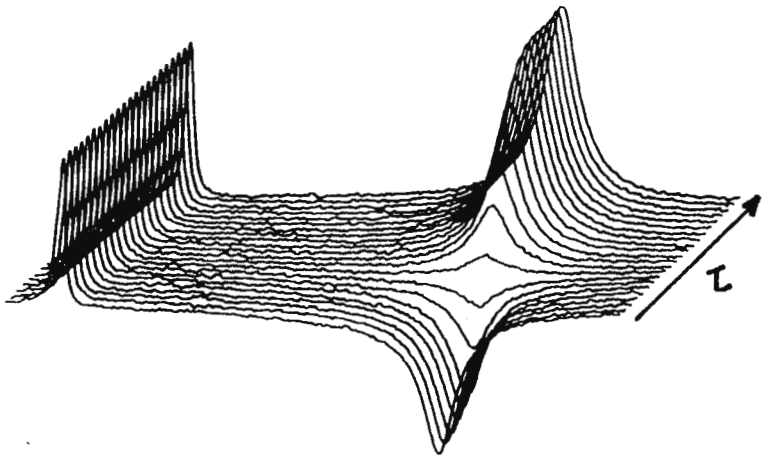
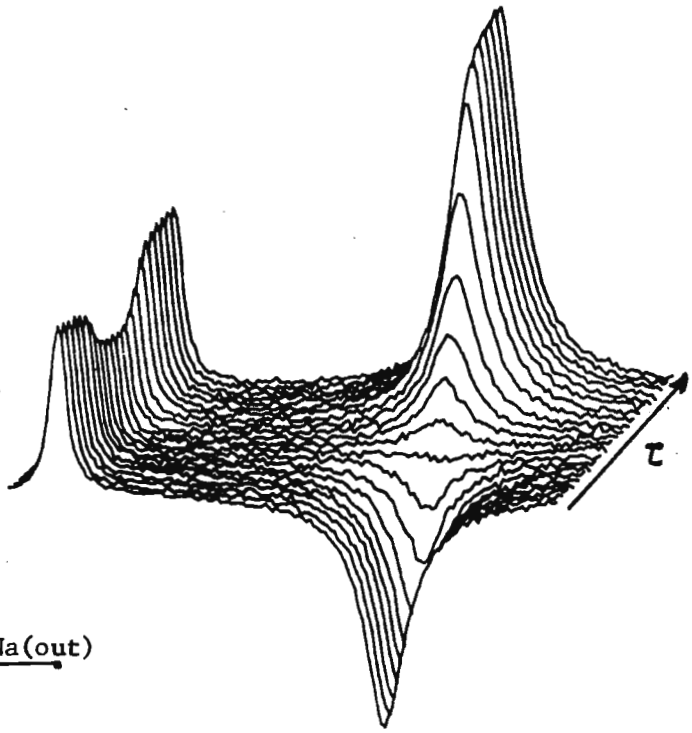


Figure 2a:

Selective inversion of Na(out) in the absence of the ionophore monensin.

Figure 2b:

Selective inversion of Na(out) in the presence of the ionophore. Note transfer of inversion to Na(in) due to transport.



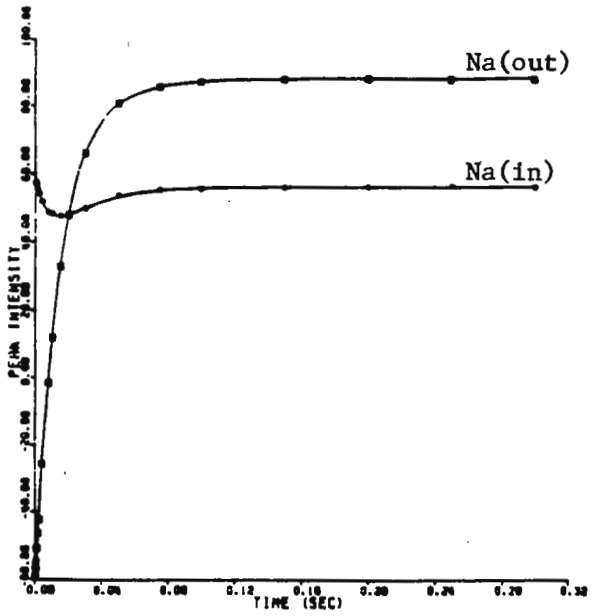


Figure 3:

Experimental (dots) and calculated curves of an inversion transfer experiment at 294 K.

Parameters:
k(in→ out): 68.5 s^{-1}
k(out→ in): 10.3 s^{-1}

Spin-lattice relaxation times:

site	measured	calculated
inside	37.1 msec	37.0 msec
outside	12.2 msec	13.3 msec

Texas A&M University NMR Newsletter - Book Reviews

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

"Modern NMR Techniques for Chemistry Research"

by
Andrew E. Derome

Pergamon Books Ltd., Headington Hill Hall, Oxford OX3 0BW, U.K., or
Maxwell House, Fairview Park, Elmsford, New York 10523, USA
1987; 280 pages; $70.00 (Hardcover), $35.00 (Softcover)

Modern NMR Techniques for Chemistry Research, by Andrew E. Derome, is perhaps the most generally useful book on high field NMR techniques for the non-specialist to appear. It admirably fills that void between the purely physical chemical, highly mathematical approach and the vague descriptive texts which offer no guidelines on actually performing experiments. The author describes his book as an introduction to modern NMR for advanced students or the researcher who wish to learn new techniques. In that regard, the book appears ideal as a text for a special topics course on NMR for graduate students. The introductory chapters (2 and 4) describe the pulse NMR model, and the other chapters are virtually independent. Chapters 5, 6, 8, 9, and 10 provide easy-to-follow discussions on NOE, polarization transfer, and selected two-dimensional experiments. Two other chapters (3 and 7) on experimental techniques are based on difficulties commonly encountered by first-time users of high field instruments. Thus, the book actually extends far beyond the demands of a text.

The style of the prose is that of a lecture illustrated with simple physical pictures to emphasize important concepts in pulse NMR without rigorous mathematical interpretation. The author is obviously aware that not all chapters of the book will be of interest to every reader and often suggests omitting certain sections. The illustrations are much more detailed than those found in other texts and depict idealized spectra as well as examples of errors.

The real value of the text to the non-specialist or first-time user of high field instrumentation is its use of real problems as examples. Chapter 5 on nuclear Overhauser effect is especially noteworthy in this regard, and the discussion of phase-sensitive COSY spectra in Chapter 8 is extremely useful. To appreciate the true value of this work to the non-specialist, however, requires one to remember that first experience with a new high field instrument. While it is true that one can learn to tune the instrument, set up data groups, etc., by a trial-and-error process, there are ways to describe these operations which could save a great deal of time, and Chapter 3 proves the point. That chapter should be included as the first 31 pages of every user's manual printed from this day forward. No NMR user or chemistry library should be without this book.

David E. Minter
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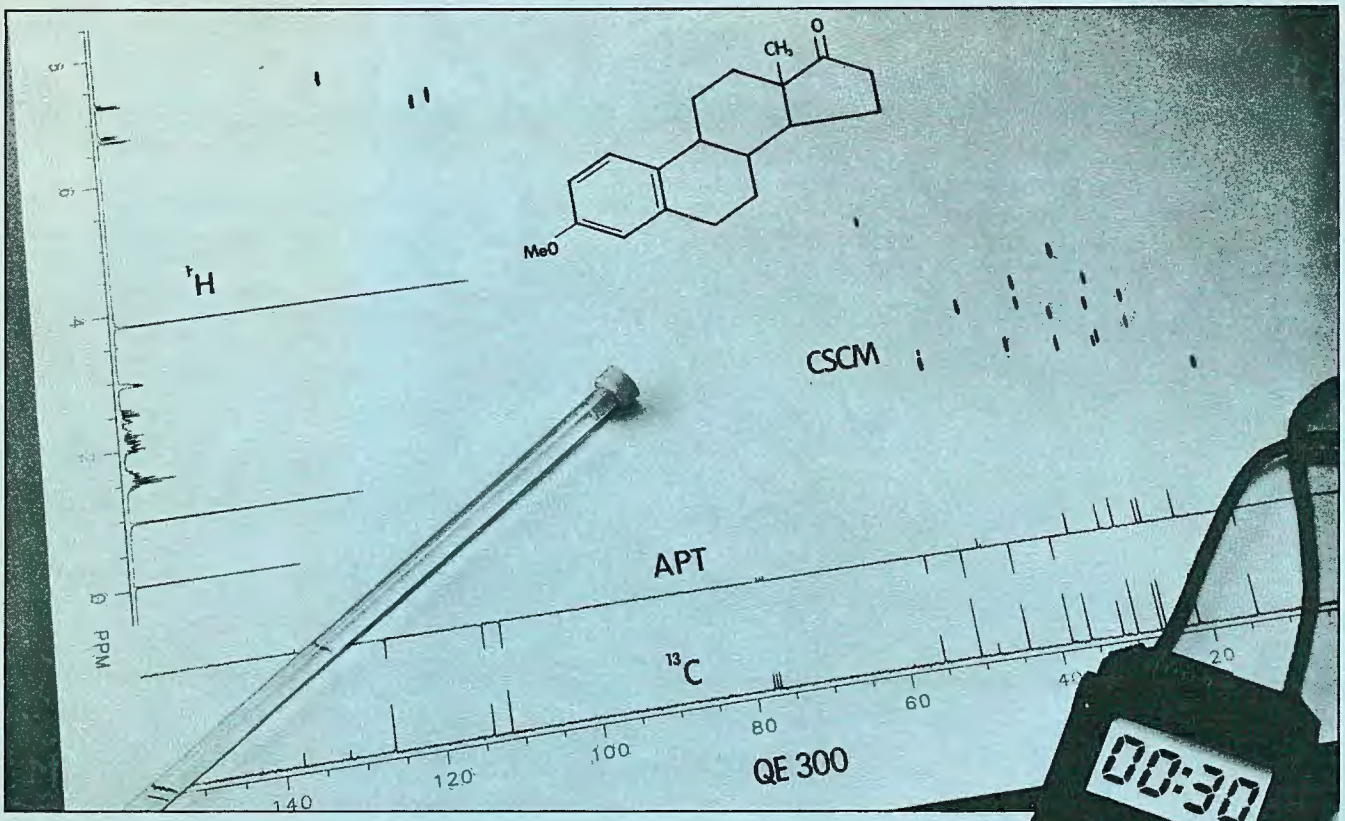

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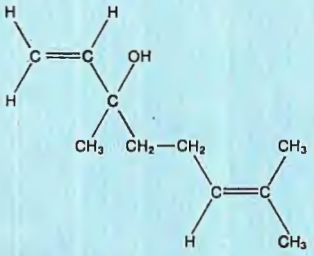

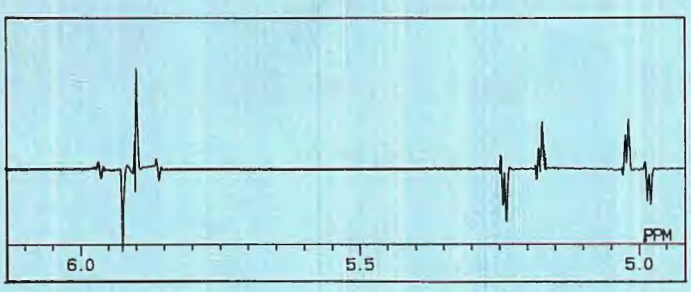

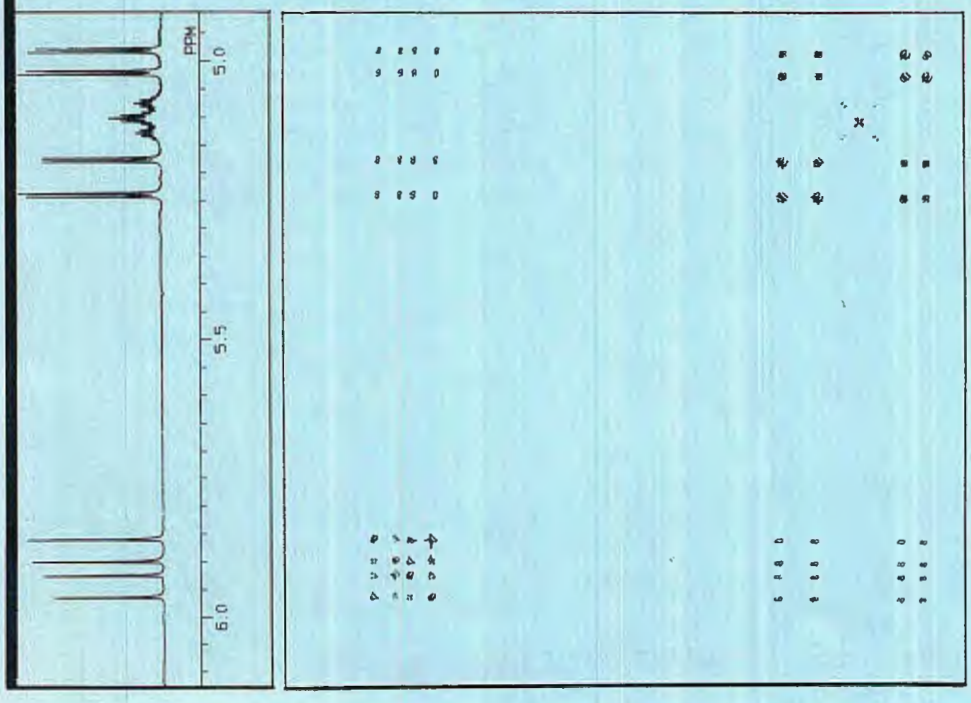

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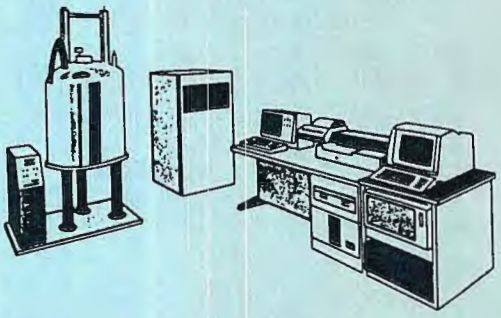

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