TEXAS A&M UNIVERSITY
NMR
NEWSLETTER

No. 368
May 1989

Continued on page 72

TABLE 1 DEUTERATED SOLVENTS

Cat. No.	Description	Formula	Min. Iso. (%D)	Density (g/cc)	MP (°C)	BP (°C)	$-\chi_v \times 10^6$ @ (°C)
D-11	Acetic Acid-d4	CH_3COOD	[illegible]	1.1[illegible]	17	[illegible]	0.551 (32)
D-120	Acetic Acid-d4 + TMS		[illegible]				
D-13	Acetone-d6	CD_3COCD_3	99.8%	0.8[illegible]	-94	57	0.460 (20)
D-121	Aceonte-d6 + 1% TMS		99.8%				
D-129							
D-14							543 (20)
D-21							0.611
D-122							
D-130							
D-28	Choloroform-d	$CDCl_3$	99.8%	1.50	-64	62	0.740 (20)
D-31	Chloroform-d + 1% TMS		99.8%				

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VARIAN

BOX/500 SHEETS

Cat. No.	Chart Size	Instrument Model	Type
WCV-100 (S-100/A)	11" X 26"	HA-100, HA-100D, HA-100D	Gridded-Two Color
WCV-60 (A-60C)	11" X 26"	A-60, A-60A, A-60A	Gridded-Two Color
WCV-XL (XL-100)	11" X 26"	XL-100 (CW and FT)	Gridded-Two Color
WCV-XLFT-100	11" X 26"	XL-100 (CW and FT)	Gridded-Two Color
WCV-XL-200	11" X 26"	XL-200, XL-300, XL-400	Gridded-Two Color
WCV-550-2	11" X 16 1/2"	EM-550	Gridded-Two Color
WCV-20 (CFT-20)	11" X 16 3/4" X 17"	CFT-20, FT-80, FT-80A All Models [illegible]	Gridded-Two Color Blank

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Varian, Analytical Instrument Division

FORTHCOMING NMR MEETINGS

Solid State NMR, June 14-16, 1989; Nijmegen, The Netherlands; Contact: Prof. Dr. Ir. W. S. Veeman; See Newsletter 368, 42.

9th International Meeting on NMR Spectroscopy, Sponsored by the Royal Society of Chemistry, July 10-14, 1989; University of Warwick, Coventry, England; Contact: Dr. John F. Gibson; (01) 437-8656; See Newsletter 364, 72.

NMR Spectroscopy *In Vivo* (Clinical Applications), July 10-12, 1989; Lyon France; Contact Prof. M. Amiel - see Newsletter 364, 73.

10th ISMAR Conference, July 16-21, 1989; Morzine (Haute-Savoie), France. (Note the newly announced location.); Contact: P. Servoz-Gavin, Departement de Recherche Fondamentale, Centre d'Etudes Nucleaires de Grenoble, B.P. 85X, 38041 Grenoble Cedex, France.

Fifth International Symposium on Magnetic Resonance in Colloid and Interface Science, August 7-11, 1989; See Newsletter 367, 57.

The Society of Magnetic Resonance in Medicine - Eighth Annual Scientific Meeting and Exhibition, August 12-19, 1989; Amsterdam, The Netherlands; Contact: The S.M.R.M. Business Office, 1918 University Ave., Suite 3C, Berkeley, CA 94704; (415)841-1899, FAX (415)841-2340.

Eastern Analytical Symposium, September 24 - 29, 1989; New York City; Contact: EAS, P. O. Box 633, Monchanin, DE 19710-0633; (302) 453-0785.

International Symposium NMR Spectroscopy: Structure and Dynamics of Polymeric Materials in the Solid State, Sponsored by the ACS Division of Polymer Chemistry, December 5-8, 1989; Keystone, Colorado; Contact: Mrs. Betty J. Schreiner, E.I. Du Pont de Nemours & Co., Experimental Station, Wilmington, DE 19880-0356; (302) 695-4817.

Spatially Determined NMR, Sponsored by the British Radiofrequency Spectroscopy Group; December 17-20, 1989; Cambridge University, U.K.; Contact: Prof. L. D. Hall, Level 4 RTC, Addenbrookes Hospital, Hills Road, Cambridge CB2 2QQ, England: (44) (223) 336805.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence Should Be Addressed To:

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

(415) 493-5971

DEADLINE DATES

No. 370 (July) ---------- 16 June 1989
No. 371 (August) ---------- 21 July 1989
No. 372 (September) ----- 18 August 1989
No. 373 (October) --- 22 September 1989

WESTERN RESEARCH INSTITUTE
P.O. Box 3395, University Station
Laramie, Wyoming 82071
(307) 721-2011

April 3, 1989
(received 4/6/89)

Professor Bernard L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

RE: ^{1}H Spin-spin Relaxation Times for Tar Sand Bitumens

Dear Barry:

The NMR activity at WRI has slowed down considerably. However, recently we were able to measure some ^{1}H spin-spin relaxation times for several tar sand bitumens. The relaxation times given in Table I were determined directly from the FID signal using an IBM PC-20 spectrometer and a Nicolet 1070 signal averager. The data are very preliminary but we hope to derive a relationship between the relaxation measurements and some physical property of the tar sand bitumens. I hope that this meager amount of information will suffice for some time until we receive funding for NMR studies on fossil fuels materials.

Sincerely,

Dan

Daniel A. Netzel

Table 1. ^{1}H Spin-spin Relaxation Times for Tar Sands Bitumens at 40°C

Phase	Asphalt Ridge	Sunnyside	Arroyo Grande
Solid-like (rigid)	12 usec	10 usec	8 usec
Solid-like (mobile)	70	49	40
Semi-liquid	270	211	242

WORKSTATION PERFORMANCE UPDATE from NMRi. April, 1989.

WHAT IS A **VUP**?

ONE **VUP** IS EQUIVALENT TO THE PERFORMANCE OF A VAX 11/780 FOR A TYPICAL MIX OF COMPUTATIONS.

NOTE:

(1) 2D FFT's REFLECT VECTOR PERFORMANCE; MOST ROUTINES ARE AT LEAST PARTIALLY SCALAR. VUPS REFLECT MOSTLY SCALAR PERFORMANCE.

(2) A FASTER CPU WITHOUT AN ARRAY PROCESSOR WILL GENERALLY OUTPERFORM A SLOWER CPU EQUIPPED WITH AN ARRAY PROCESSOR.

Workstation	SpecStation Model	SpecStation Approx. Cost[1] ($k)	VUP's	1kx2k 2D Processing (minutes)[2,3]	Typical 12 Peak Curve Fit (minutes)[3]	SpecStation Availability
VAXstation II/GPX	S/1012 (not current)		0.9	20	ca. 10	discontinued
VAXstation 3100	S/1021	$55–65	2.7	7	3–5	now
DECstation 3100	S/1030	$65–70	14	<2	0.5	available 5/89
Sun 386i/250	S/2001	$40–50	3	5	3–5	available 7/89
Sun 3/60FC	S/2030	$50–60	10	3	~1	now
Sun 4/110 w/new FPA	S/2021X	$70–80	10	3[4]	~1	available 5/89
Sun 4/330	S/2032	$75–90	15	<2[4]	<1[4]	available 8/89
w/ Sky Warrior IIAP	S/2032AP	$95–115	18	~0.5[4]	<1	available 9/89
Silicon Graphics 4D/20G	S/5005	$70–80	10	<2[4]	1[4]	available 6/89
Stellar GS1000	S/3000	$150–175	>25	0.3	0.25	available 7/89
Ardent Titan-2	S/4002	$130–160	>25	0.3[4]	0.25[4]	available 6/89

[1] With ca. 300 MB disk, cartridge tape, color graphics system, printer, plotter, accessories, software.
[2] Starting from 256 x 2k dataset.
[3] Estimated for several systems, where the software porting is underway.
[4] Anticipated.

Note: VAXstation models can be ordered with VMS for access to the thousands of programs available on VMS. The UNIX workstations also support a variety of chemical applications. For further information, call NMRi.

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Prof. Dr. F. H. Köhler
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DER
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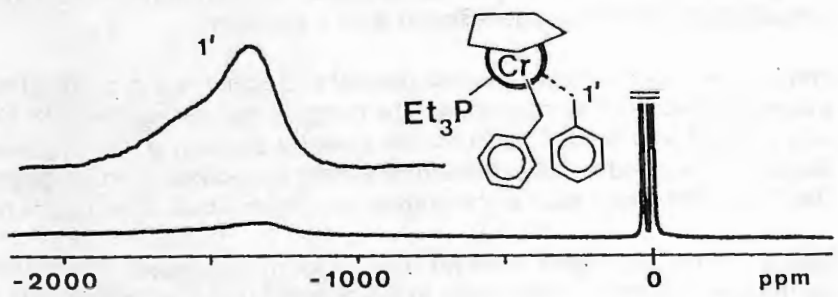
Lichtenbergstraße 4
Ruf-Nr. (089) 3209- – 3109
Telex: 17898174
Teletex: 898174

20.02.1989
(received 3/28/89)

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

$^{1/2}$H NMR signals with shifts >1000 ppm

Dear Dr. Shapiro,
many fascinating molecules escape the attention - or at least the appropriate scientific care - of organometallic chemists because they are paramagnetic and quite some publications state that "NMR spectra cannot be obtained due to unpaired electrons". But even those who routinely record spectra of such compounds have much to put up with missing signals. This is especially annoying when the experimental conditions are very good (sensitive nucleus like ^{1}H and hundreds of milligrams in the NMR tube) and when the potential chemistry associated with the molecule stimulates the effort.
Paramagnetic transition metal alkyl derivatives belong to this category. For instance, we were unable to detect the underlined protons of $CpCr(C\underline{H}_2R)_2(PR'_3)$ ($Cp = C_5H_5$) and similar compounds. These protons are most interesting with regards to the bonding in and the thermochemistry of these molecules. We have overcome the problem by substituting protons for deuterons and recording ^{2}H NMR spectra; an example is given below.



All compounds give signals with high frequency shifts in a range of 1200 - 1500 ppm and line widths of 1900 - 6200 Hz. It is clear then that the corresponding proton signals should be very difficult to detect because they are expected to be up to 260 kHz broad. It is true that in the ^{2}H NMR spectra the signals are still broad, however, due to the large shifts they are rather well separated. For instance, in the figure the resonances of the diastereotopic deuterons have a shift difference of 170 ppm.
May be that these values are records (may be also that your readers know larger values - comments are welcome), the essential point is that now it is easy to identify the hydrogen atoms which are separated by two bonds from a paramagnetic metal center and to follow the fate of the ligand (especially methyl) during a reaction. Details of this work will appear in Chemische Berichte.

Yours sincerely,

(F. H. Köhler) (H. Zeh)

StonyBrook

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794-3400
PHONE NO: 516 632-7923 **FAX NO:** 516 632-7960

March 20, 1989
(received 3/22/89)

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

Re: Magnetic Susceptibility Shift Selective Imaging: MESSI

Dear Barry:

In biological tissue, compartmental differences in bulk magnetic susceptibility (BMS) lead to frequency shifts in magnetic resonance experiments. These shifts can give rise to distortions in MR spectra and/or images of such samples. Recently, we have reworked and organized the theory of the BMS frequency shift.[1] Here, we offer perhaps the simplest example of this effect and suggest a way to exploit it to advantage.

In part a of the Figure, we show the ^1H spectrum of a phantom sample obtained with a Bruker 40 cm bore 4.7 T BIOSPEC instrument. The sample consisted of an 85 mm long glass cylinder, 41 mm in diameter, positioned with its axis colinear with that of the magnet (Z). This cylinder had two smaller glass cylinders, each 10 mm in diameter, built into it. One occupied a diameter of the large cylinder which lay in the XZ plane (Y is vertical) and was thus perpendicular to $\mathbf{B}_0$. The axis of the other small cylinder (45 mm long) was colinear with that of the large cylinder and was thus parallel to $\mathbf{B}_0$. The two small cylinders were filled with distilled water and the large cylinder was filled with air. The spectrum consists of two homogeneous resonances because the volume BMS of distilled water (-9.1 ppm) is different from that of air (ca. 0 ppm).[1] The small spectral inhomogeneities observed are due to $\mathbf{B}_0$ inhomogeneities and the fact that the small cylinders are not infinitely long. The higher frequency resonance is due to the water in the perpendicular cylinder while that at lower frequency arises from the water in the parallel cylinder. The splitting between them would be 4.5 ppm if the cylinders were aligned perfectly perpendicular and parallel to $\mathbf{B}_0$, respectively.[1] If the large cylinder was also filled with distilled water, a single homogeneous resonance would be observed at the position of the lower frequency peak of the spectrum in part a. The presence of the relatively thin glass (BMS, ca. -10.7 ppm) walls of the smaller cylinders would cause unnoticeably small inhomogeneities in such a spectrum.

Part b of the Figure shows a midline coronal (XZ plane) image of the phantom sample obtained with a standard spin echo imaging pulse sequence. The image is distorted by the BMS frequency shift. For example, since the read gradient was in the Z direction, the spatial separation of the images of the two small cylinders in the Z direction is modified.[1] Such a distortion cannot be avoided in an image produced from the entire spectrum. The image distortions seen at the ends of the perpendicular cylinder are due to its finite length.

Parts c and d of the Figure show MESSI images of the sample. These were produced by selecting the high and low frequency signals, respectively, in the absence of field gradients. We have achieved such images with more than one frequency selection pulse sequence. Besides producing edited images, these experiments can yield images undistorted by the BMS frequency shift if the reference frequency is sequentially centered at the position of each selected peak.

We have submitted a communication describing MESSI experiments using a phantom sample more representative of tissue.[2] This work shows how image contrast can be achieved from the BMS frequency shifts (as distinct from relaxation enhancements) caused by the infusion of a nontoxic vascular paramagnetic reagent.

Best regards,

Charlie

Charles S. Springer, Jr.
Professor

Yan Xu
Research Assistant

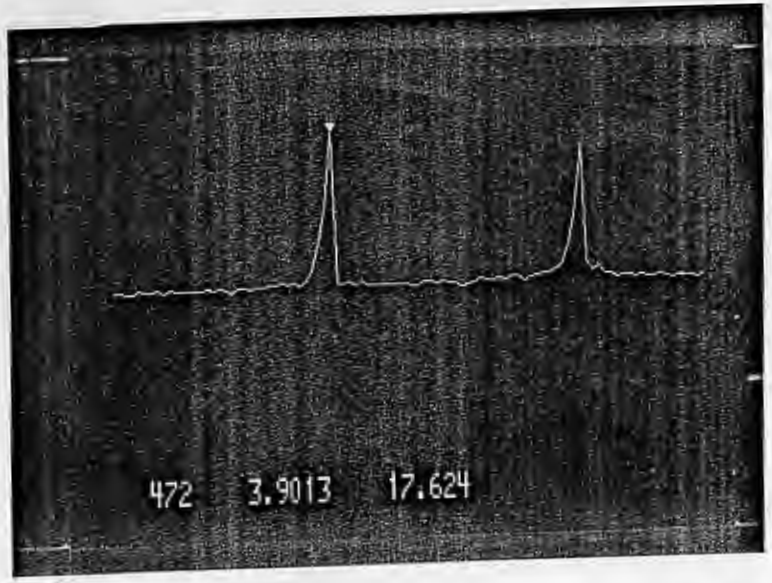
Jim Balschi

James A. Balschi
Assistant Professor
University of Alabama
Medical School

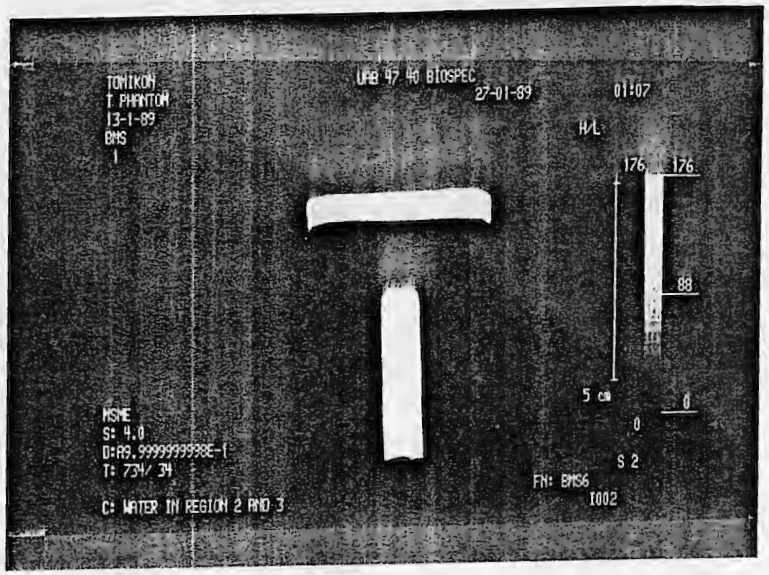
1 S.C-K. Chu, Y. Xu, J.A. Balschi, and C.S. Springer, *Magn. Res. Med.*, in press.
2 Y.Xu, J.A. Balschi, and C.S. Springer, submitted for publication.

P.S. We at Stony Brook are pleased to welcome George Crull as the new Departmental NMR Coordinator.

a)


472 3.9013 17.624

b)


TOMIKON
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176
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MSME
S: 4.0
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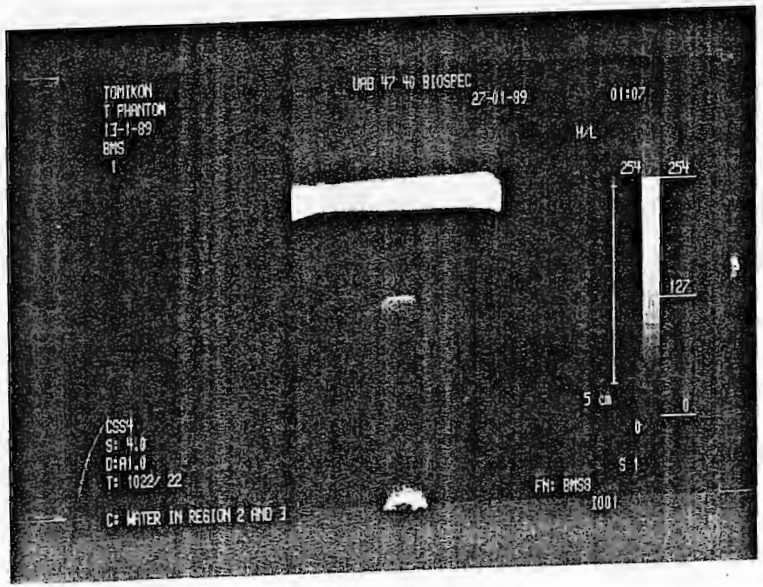
T: 734/ 34
C: WATER IN REGION 2 AND 3

c)


TOMIKON
T PHANTOM
13-1-89
BMS
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UAB 47 40 BIOSPEC
27-01-89
01:07
H/L
254
254
127
5 cm
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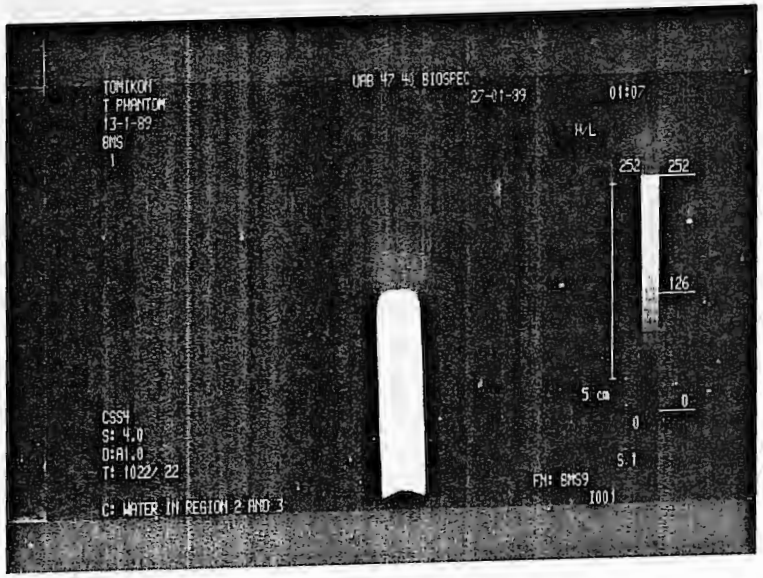
0
S 1
FN: BMS8
I001
CSS4
S: 4.0
D:A1.0
T: 1022/ 22
C: WATER IN REGION 2 AND 3

d)


TOMIKON
T PHANTOM
13-1-89
BMS
1
UAB 47 40 BIOSPEC
27-01-89
01:07
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252
126
5 cm
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S 1
FN: BMS9
I001
CSS4
S: 4.0
D:A1.0
T: 1022/ 22
C: WATER IN REGION 2 AND 3

IBM
T. J. Watson Research Center
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Yorktown Heights, NY 10598
914-945-1356
Bitnet: JWCNMR @ YKTVMV

March 23, 1989
(received 3/27/89)

Dr. Barry Shapiro
TAMUNMR Newsletter
966 Elsinore Ct.
Palo Alto, CA 94303

Dear Barry:

"Making ASCII files from PCNMR files"

Here at Yorktown, we have PCNMR running in several offices and a server PC-XT in the lab hooked to our AF-250 spectrometer. Using the software that we developed in conjunction with Bob Johnson and Sean Philpott at IBm Almaden Research, we can now transfer the data to the PC and automatically upload it to a disk on our mainframe network. From this point, we can down load it to any office workstation as well as work on the data on the host.

This has led to the question regarding the format of PCNMR data files. It is sometimes desirable to be able to convert the data to ASCII so that it can be processed by host-based FORTRAN programs. The data are stored as 32-bit signed integers starting 2560 bytes (640 long words) into the file. Thus, a simple QuickBASIC program can be used to write out an ASCII file which can be uploaded to the host machine for further processing:

```
'Simple program to read in PCNMR data file and write out ASCII file
'------J.W. Cooper 3/89 ------------
CONST OFFSET = 2560                          'offset is start of data in bytes
DIM x AS LONG, ptr AS LONG                   'reserve long integer variables

OPEN "glupent.001" FOR BINARY AS #1          'open binary file
OPEN "glupent.asc" FOR OUTPUT AS #2          'open ASCII file
specsize = (LOF(1) - OFFSET) / 4             'calculate file size
FOR i = 1 TO specsize                        'read in data points
   ptr = OFFSET + (i - 1) * LEN(x) + 1       'calculate posn of data in file
   GET #1, OFFSET + ptr, x                   'get each data point
   PRINT #2, i, x                            'print out into ASCII file
NEXT i
CLOSE #1                                     'close spectrum file
CLOSE #2                                     'and close the ASCII file
END
```

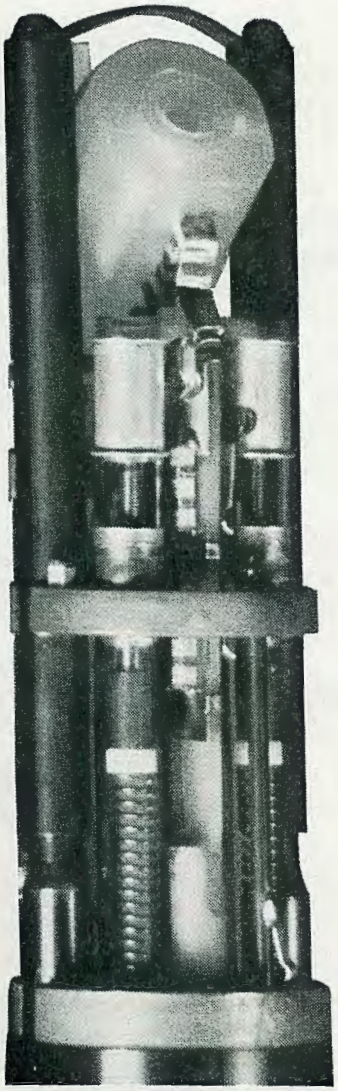
The above program does exactly that.

Best regards,

Jim Cooper

James W. Cooper,
Research Staff Member,
Laboratory Automation

Doty Scientific, Inc.



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Fast Flipping Variable Angle probes for DAS 30° to 90°.

Fiber optics spin detection.

Triple tuned probes.

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High temperature MAS probes to 700 °C.

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Note - Prices on this page do not include the necessary starter kits

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Ultra high speed (5 mm - 14 kHz, 7 mm - 9 kHz)	3,500.
Multinuclear Observe Channel (Complete multinuclear capability using plug in capacitor "wands", can provide continuous coverage from ^{31}P to ^{103}Rh in a single probe)	2,500.
Capacitor wands (each)	200. to 600.
Adders for higher field probes:	
250 MHz to 350 MHz	500.
360 MHz to 400 MHz	1,000.
500 MHz	1,500.
600 MHz	2,000.
Fast flipping variable angle (30° to 90°)	1,500.
Stepper Motor and controller for DAS (Variable angle not available on all probes)	3,500.
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Additional Features:	
Multinuclear	1,500.
Triple Tuned	2,500.
CRAMPS Probe: Single tuned VT probe ^{1}H or ^{19}F	
8 kHz 5 mm MAS, 1.5 μs 90° pulses	10,500.
High Temperature MAS Multinuclear Probe: -100 °C to +700 °C (7 mm only)	
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March 27, 1989.
(received 4/7/89)

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

Electronic substituent effects on two-bond DHIECS values in 5-substituted indoles.

Dear Professor Shapiro:

The two-bonds deuterium/hydrogen NMR isotope effects on ^{13}C chemical shifts (DHIECS) resulting from partial deuterium exchange at the NH site in a series of eleven 5-substituted indoles, measured as 0.83 M solutions in DMSO-d_6 are given in Table 1, as well as the Hammett--type σ parameter[1] and the corresponding $^1H(NH)$ and ^{15}N chemical shifts[2].

The dependence of $^2\Delta$ DHIECS values on the electron density at the hydrogen (deuterium) atom is evidenced on the basis of a series of least-squares correlations described in equations 1-6 on Table 2. In DMSO, the NH proton is engaged in a hydrogen bonding with the solvent[3,4]; however this fact do not obscures the overall pattern of electronic substituent effects, as is illustrated by the excellent or good correlations between either $\delta^1H(NH)$, $\delta^{15}N$ or the average of $^2\Delta$ DHIECS parameters with the σ values (eq. 1-3, Table 2).

A parallel behavoir of the ^{15}N chemical shifts and the $^1H(NH)$ proton shifts indicates that the substituents at C-5 have a qualitatively similar effect on both of these chemical shifts; electronegative substituents produce a downfield shift in each case whereas electron-donating groups induce shifts to higher fields. A least-squares plot of the ^{15}N chemical shifts versus the $^1H(NH)$ chemical shifts illustrates this correlation (eq. 4, Table 2).

If electron density at the hydrogen (deuterium) atom directly influences the magnitude of $^2\Delta$ DHIECS values, then one would expect them to depend on the $^1H(NH)$ chemical shift in the same way as the $^1H(NH)$ chemical shift varies with electronic substituent effects. Our results show that the average of $[^2\Delta(C2 + C7a)]/2$ provides a good correlation with the $^1H(NH)$ chemical shift (eq. 5, Table 2). Also, a dependence between the average of the $[^2\Delta(C2 + C7a)/2]$ DHIECS values with the ^{15}N chemical shift is present (eq. 6, Table 2). These results clearly indicate that $^2\Delta$ DHIECS values are sensitive to changes in the electronic environment in a predictable manner and their magnitudes increase when the electron density at the hydrogen (deuterium) atom decreases.

The DHIECS values were determined from mixtures of deuterated and isotope-free material on a Varian XL-300GS spectrometer at 75.4 MHz.

Table 1

Hammett-type σ values and NMR parameters for 5-substituted indoles in DMSO[a].

Substitutent	σ[b]	δ^1H(NH)[c]	δ^{15}N[d]	[$^2\Delta$ C2]	[$^2\Delta$ C7a]	[$^2\Delta$(C2+C7a)]/2
NO_2	0.80	11.89	-234.2	168.8	165.5	167.15
CN	0.69	11.73	-	167.2	161.7	164.45
CO_2Me	0.44	11.53	-	165.6	161.7	163.65
Br	0.25	11.33	-239.4	166.6	157.9	162.25
Cl	0.23	11.31	-239.6	167.0	156.4	161.70
F	0.16	11.21	-	168.0	153.9	160.95
OAc	0.08[e]	11.17	-	164.8	155.6	160.20
H	0	11.08	-241.1	163.6	156.2	159.90
Me	-0.15	10.92	-241.9	164.7	154.2	159.45
OMe	-0.18	10.92	-242.4	165.9	151.9	158.90
NMe_2	-0.46	10.70	-	166.1	150.9	158.50

[a] $^2\Delta$ DHIFCS values in ppb (10^{-9}) at 75.4 MHz; [b] from ref. 1; [c] in ppm, at 300 MHz; [d] ppm upfield from[2] external HNO_3; [e] calculated from eq. 1, Table 2 using 10 points.

Table 2

Least-squares correlations of nmr parameters for 5-substituted indoles and their correlation coefficients (r).

equation	y	=	m	x	+	b	r
1	δ^1H(NH) ppm		0.95	σ		11.09	0.998
2	δ^{15}N ppm		8.15	σ		-241.06	0.993
3	[$^2\Delta$(C2+C7a)]/2 ppb		6.81	σ		160.40	0.964
4	δ^{15}N ppm		8.11	δ^1H(NH) ppm		-330.96	0.993
5	[$^2\Delta$(C2+C7a)]/2 ppb		7.22	δ^1H(NH) ppm		80.26	0.977
6	[$^2\Delta$(C2+C7a)]/2 ppb		1.02	δ^{15}N ppm		405.10	0.998

1.- S. Ehrenson, R.T.C. Brownlee and R. Taft, Phys. Org. Chem., 10, 13 (1973).

2.- E. Rosenberg, K.L. Williamson and J.D. Roberts, Org. Magn. Reson., 8, 117 (1976).

3.- I. Harada, T. Miura and H. Takeuchi, Spectrochim. Acta, 42 A, 307 (1986).

4.- A. Lautié, M.F. Lautié, A. Gruger and S.A. Fakhri, Spectrochim. Acta, 36 A, 85 (1980).

Sincerely yours,

M.S. Morales Ríos

Pedro Joseph-Nathan

UNIVERSITE DES SCIENCES ET TECHNIQUES DU LANGUEDOC

GROUPE DE DYNAMIQUE DES PHASES CONDENSEES

Unité de Recherche Associée au C.N.R.S. n° D 0805

Montpellier, on February 24, 1989
(received 4/6/89)

Dear Pr. Shapiro,

"13C NMR investigation of the plastic-solid phase transition in plastic crystals mixtures"

Plastic crystals like PG (2-hydroxymethyl-2-methyl-1,3-propanediol) and NPG (2,2-dimethyl-1,3-propanediol) experience a solid (crystal phase) to solid (plastic phase) transition at temperature 80°C and 38°C respectively. By making homogeneous mixtures of these compounds one expects to control the transition temperature. For instance calorimetric measurements show that this temperature becomes 58°C for a 80% PG - 20% NPG mixture. By looking at the 13C NMR of the various sites of the molecules we can investigate in detail the appearance of the plastic phase at the molecular level during a thermal treatment of such a mixture. On Figure 1, we present the high resolution 13C NMR spectra of this mixture obtained using classical CP-MAS techniques. The room temperature spectrum is equivalent to the superposition of both PG and NPG spectra in their solid phase. At high temperature (T>350°K) the spectrum is also equivalent to the superposition of both PG and NPG spectra in their plastic phase. Our results show that both spectra characteristics of the plastic phase for the two components PG and NPG appear at the same time during the thermal evolution.

This observation allows us to conclude that such a mixture behaves like an homogeneous system and that the transition temperature is mainly determined not by the nature of the molecule but by its environment. Relaxation times measurements on the various carbon sites are under progress to study in detail the molecular kinetics around the transition temperature.

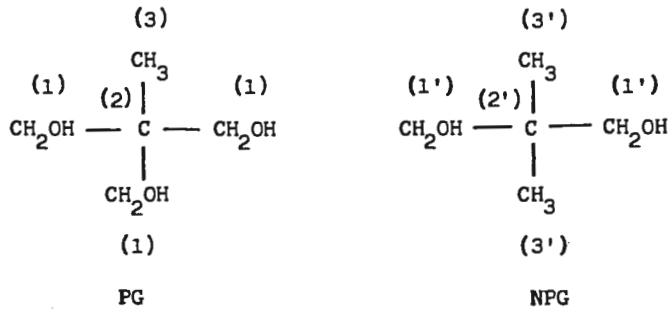
Yours sincerely,

P.BERNIER M.RIBET F.WILMET

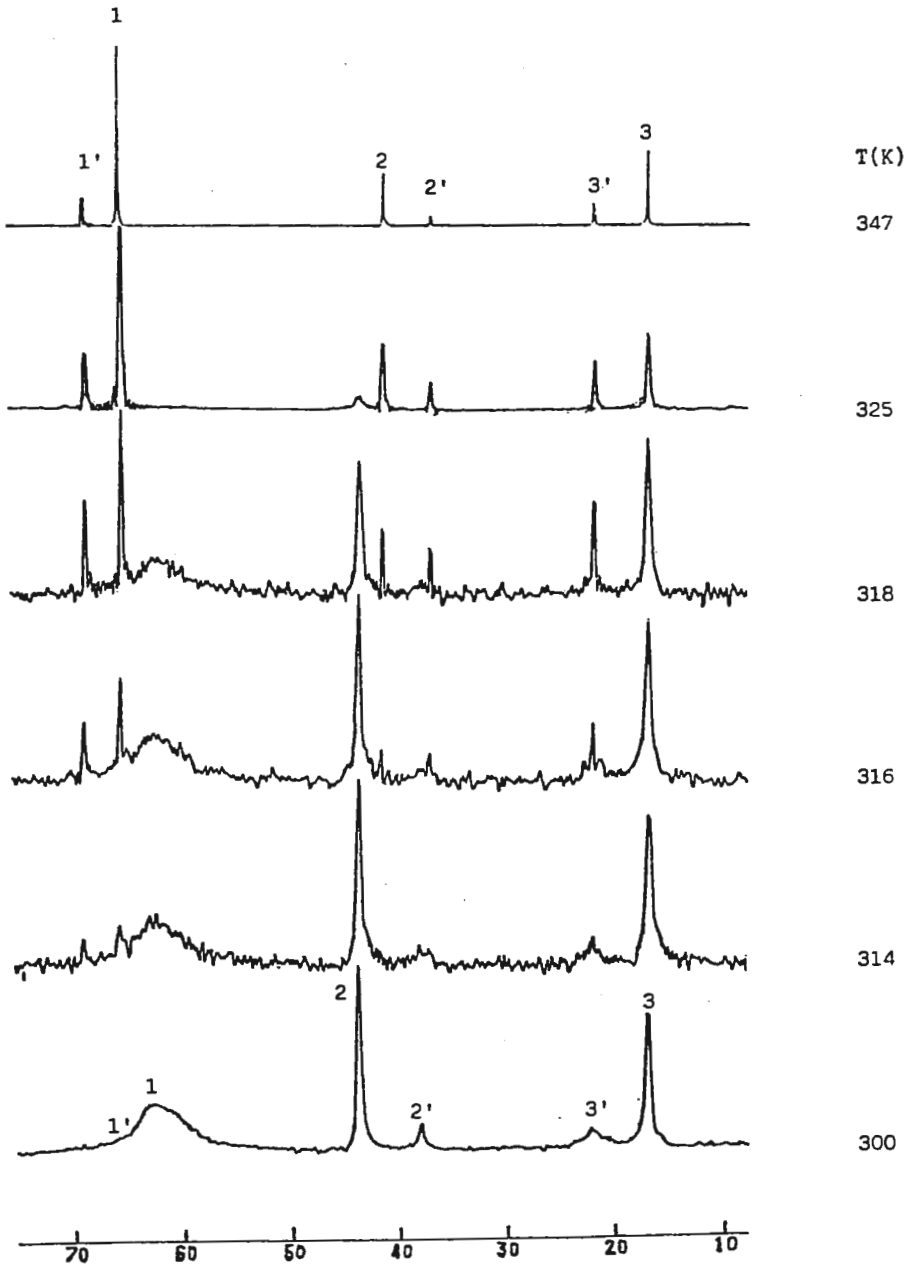
P.BERNIER, M.RIBET, GDPC/USTL, 34060 Montpellier Cedex.

F.WILMET, L.ELEGANT, Laboratoire de Thermodynamique Expérimentale
Parc Valrose, 06034 Nice.

Y.GIRAULT, Laboratoire de Chimie Physique Organique, 06034 Nice.



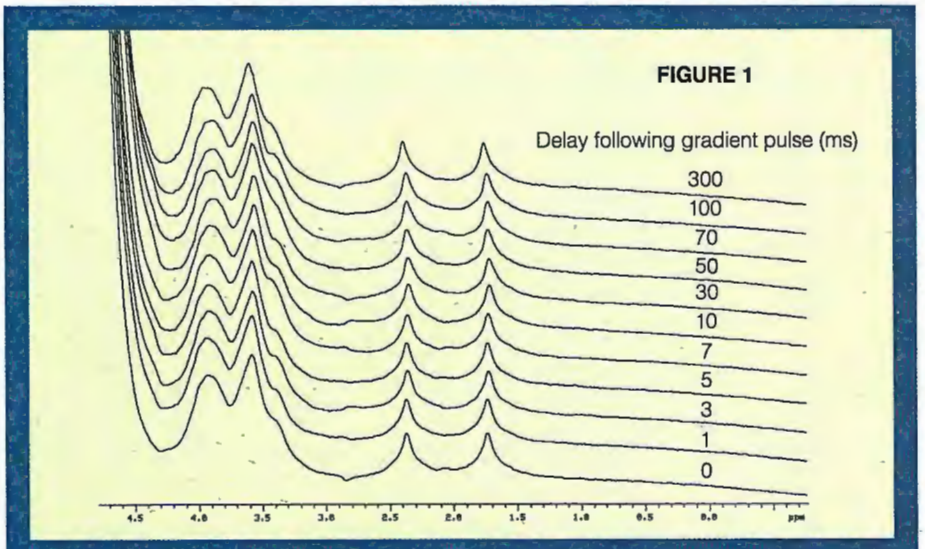
PG(80%) - NPG(20%)
^{13}C NMR

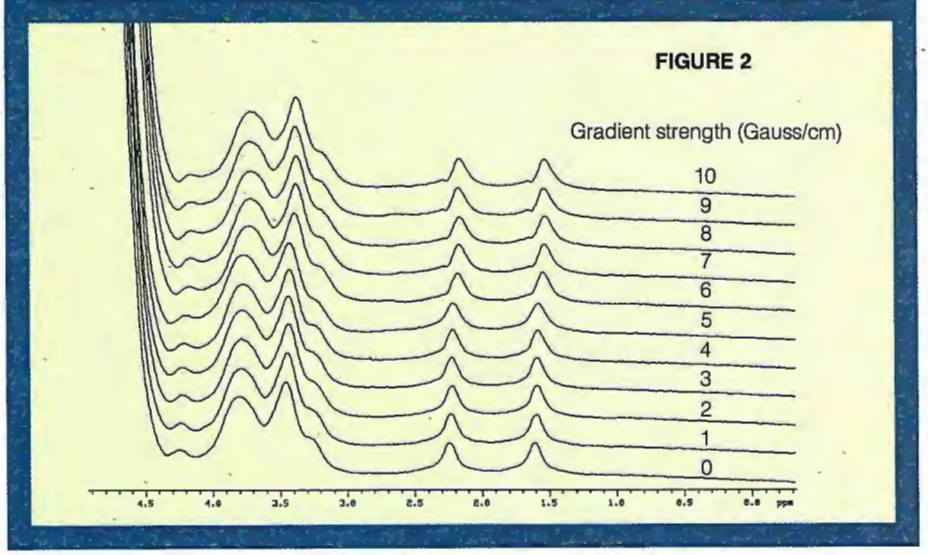


High Performance Auxiliary Gradient Coils

Dedicated RF coils, optimized for a specific application or a particular sample or both, have long been a tradition in NMR imaging as well as NMR spectroscopy. Similarly, dedicated gradient coils yield dramatic performance improvements in terms of rise and fall times, maximum gradient strength, duty cycle and eddy currents. Sophisticated eddy current compensation techniques reduce any residual spatial or temporal field variations due to eddy currents to a few hundredths of a percent, thus yielding distortion free spectra and images.

At Spectroscopy Imaging Systems we are able to obtain in-plane resolution of $20\mu \times 20\mu$ in an axial cut through an okra of 1.3 cm diameter. (See image shown on front side.) An enlargement of a portion of a seed capsule within the okra displays a wall thickness of 50μ (inset on front side). The gradient coil used to obtain this excellent performance has a diameter of 125 mm and was mounted in an Oxford Instruments 4.7 Tesla, 330 mm bore magnet without removing the standard set of gradient coils. The auxiliary gradient set is capable of generating greater than 10 Gauss/cm in all orientations using the same gradient power supply as the primary gradient coil.





The excellent control of eddy currents using the smaller gradient insert is demonstrated in Figures 1 and 2. Figure 1 shows a series of spectra of the high field region of a sample containing [2-^{13}C] acetate and [1-^{13}C] glucose in H_2O/D_2O. With the sample in the center of the gradient coil, a 1 second gradient pulse of 1 Gauss/cm was applied. The gradient pulse was followed by a variable delay, a 90° RF pulse and acquisition of the resultant free induction decay. All spectra are essentially undisturbed even at delay times below 10 ms.

Figure 2 shows a typical series of spectra of the same sample at an off-center location in the magnet. A gradient pulse of 5 ms duration with an amplitude range of 0 to 10 Gauss/cm was applied, and the FID recorded at a fixed delay time of 3 ms. The sample was positioned at 22.3 mm off the center, corresponding to local gradient field of 95 kHz. All spectra are virtually undisturbed, even at 10 Gauss/cm.

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DEPARTMENT OF CHEMISTRY
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SUNCOM: 574-2144

March 28, 1989
(received 4/6/89)

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

Dear Barry:

As most software addicts who are also NMR spectroscopists are no doubt aware, I have spent a great deal of my (spare!) time writing software usable by NMR spectroscopists for their everyday needs. Over the last few years, I have corresponded with quite a few people who use the software I have generated and who, for the most part, seem to be quite gratified with my basic philosophy: "Write the software, give the listings, and let the user improve upon what he has been given if he can."

In light of the above philosophy, I now submit yet another computer program. This one is called "COSYSIM." What this program does is two things:

1) Generates stick spectra given chemical shifts and coupling constants ("weak coupling" approximation).
2) Generates COSY (2D) NMR spectra from the given stick spectrum.

Both things, as outlined above, are fairly routine but I have noticed that people distributing software are rather reluctant to give their listings (*i.e.,* show how their software is written). This is *not* my philosophy. Anyone desiring COSYSIM need only send me a 5.25" disk (360K or 1.2M format) or a 3.25" disk (720K or 1.44M format) and I shall be glad to return the programs to that person. The program runs on an IBM-PC or IBM-PS2 or clone. When sending your disk please *be sure* to let me know which format you request!

Now, we look at a sample output of the program. First, we examine a stick plot output, as shown in Fig. 1. Then, we look at the COSY spectrum for this stick spectrum as shown in Fig. 2. This presentation is not as "pretty" as one would expect from a full 8.5" x 11" output. Nevertheless, it should be *more than adequate* to give an idea of the program's capabilities.

Figure 1. Stick plot of a rather complicted spin system which is, nevertheless, weakly coupled.

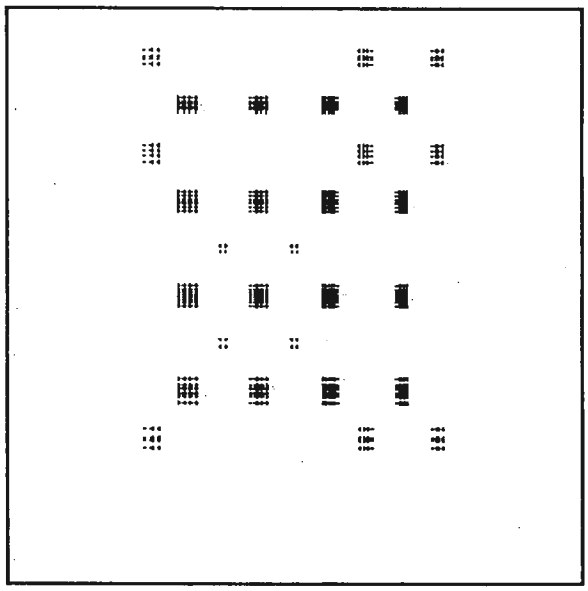

Figure 2. COSY spectrum corresponding to the stick plot of Fig. 1.

The program which produced these spectra also requires a VGA monitor. If the user does not have this, he should be able to easily change the code to allow the program to run on a system with a CGA or EGA monitor. In any event, it is hoped that this program will prove fun and useful to a large number of NMR people.

Sincerely yours,

Milt

Milton D. Johnston, Jr.
Associate Professor
Metaphysical Chemistry

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COLLEGE OF ARTS & SCIENCES

FACULTY OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY

April 17, 1989
(received 4/21/89)

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

*Re: **Ab Initio Calculations of Chemical Shielding in Transition Metal Complexes***

Dear Barry:

For some time we have been interested in seeing how well the distributed origins approaches (e.g., the IGLO[1] and LORG[2] methods) for calculations of chemical shielding would work for transition metal complexes for which there is a vast amount of poorly understood experimental data. To the best of our knowledge there have been only two papers [3] reporting ab initio calculations in metal systems, and these used the nucleus as origin, a procedure that led to most of the poor data prior to the introduction of the distributed origins methods. Moreover, except for a few compounds of Mn, their calculations were for metals having d^{10} configurations for which the diamagnetic terms would provide the major contributions. Clearly, it was of interest to compare the results of the distributed with the non-distributed origins calculations for these compounds.

Table I includes some of our shielding results for Zn and Cu as well as their decomposition into diamagnetic and paramagnetic contributions. Also included are the results of Nakatsuji et al [3] and some very uncertain experimental data. Most of the IGLO and LORG/GAUSSIAN86 results are in reasonable correspondence with the data published previously. The quantitative differences are attributable to the basis sets. In addition, we used total or partial geometry optimization since there tend not to be gas phase experimental data for these molecules. A major difference does occur for the CuCl molecule in Table I wherein we obtain a shielding value of +2273 ppm via the LORG algorithm (+2440 ppm using the IGLO method) versus -2246 ppm reported by Nakatsuji. Based on a calculation with a similar basis set, it appears that the large paramagnetic term leading to the latter value was due to spurious convergence to a d^8 rather than a d^{10} configuration. Also, it is inconsistent with all of their other results.

The conclusions that one might draw from all of this is that (at least for highly symmetrical and/or essentially ionic molecules in which the paramagnetic terms are small) the distributed and non-distributed origins methods lead to comparable results if the basis sets are similar, and care should be used in their selection

to assure convergence to the correct configuration. Our results indicate that substantial contributions to the paramagnetic terms are due to the orbitals directly involved in the chemical bonding. In the case of CuCl and $ZnCl_2$ the d-orbitals contribute only -43 and -65 ppm, respectively to the total paramagnetic contributions.

Table I. Chemical Shielding Based on the LORG/GAUSSIAN86 Procedure Compared with FPT Results and Experimental Data for Several Zinc and Copper Complexes[a,b]

Molecule	σ_d	σ_p	σ_T	δ(LORG)[c]	δ(FPT)[c]	δ_{exp}[c,d]
$[Zn(H_2O)_6]^{2+}$	2350	- 50	2300	0	0	0
$[ZnCl_4]^{2-}$	2306	- 90	2216	- 84	- 156	-253
$ZnCl_2$	2354	-212	2142	-158	- 257	-295
$[Zn(CN)_4]^{2-}$	2345	-237	2098	-202	- 472	-284
CuCl	2352	- 79	2273	-	(-2246)[e]	-

[a] All values are in ppm· b Basis sets (3-21G) on the ligands, (53321/5311/41) on Zn and Cu. [c] Values of the chemical shifts are referenced to $[Zn(H_2O)_6]^{2+}$. [d] Experimental data from Maciel et al, J. Phys. Chem, **1977**, 81,263. [e] Calculated value of σ_T from ref[3].

Work on transition metal systems with partially filled d-orbitals is of primary interest; we have completed some calculations which reproduce the experimental trends for a series of molybdates and thiomolybdates. This will be submitted for publication in the near future.

We wish to extend thanks to Professor Tom Bouman for providing a preliminary version of the RPAC program, which contains the LORG algorithm, and to Professor W. Kutzelnigg for permission to use the IGLO program. We are indebted to Dr. Julio Facelli of the University of Utah; his help was essential in getting these programs operational. We are also want to express our appreciation for support from the U. S. Department of Agriculture and the Cornell National Supercomputer Facility.

Sincerely yours,

Jaime Combariza Mike Barfield

[1] Kutzelnigg, W. Israel J. Chem. **1980**, 19, 193. Schindler, M.; Kutzelnigg, W. J. Chem. Phys. **1982**, 76, 1919. Schindler, M.; Kutzelnigg, W. J. Am. Chem. Soc. **1985**, 105, 1360. [2] Hansen, A. E.; Bouman, T. D. J. Chem. Phys. **1982**, 82, 5035. Bouman, T. D.; Hansen, A. E.; Voigt, B.; Rettrug, S. Int.J.Quantum Chem., **1983**, 23, 595. [3] Nakatsuji, H.; Kanda, K.; Endo, K.; Yonezawa, T. J. Am. Chem. Soc. **1984**, 106, 4653. Kanda, K.; Nakatsuji, H.;Yonezawa, T. J. Am. Chem. Soc. **1984**, 106, 5888.

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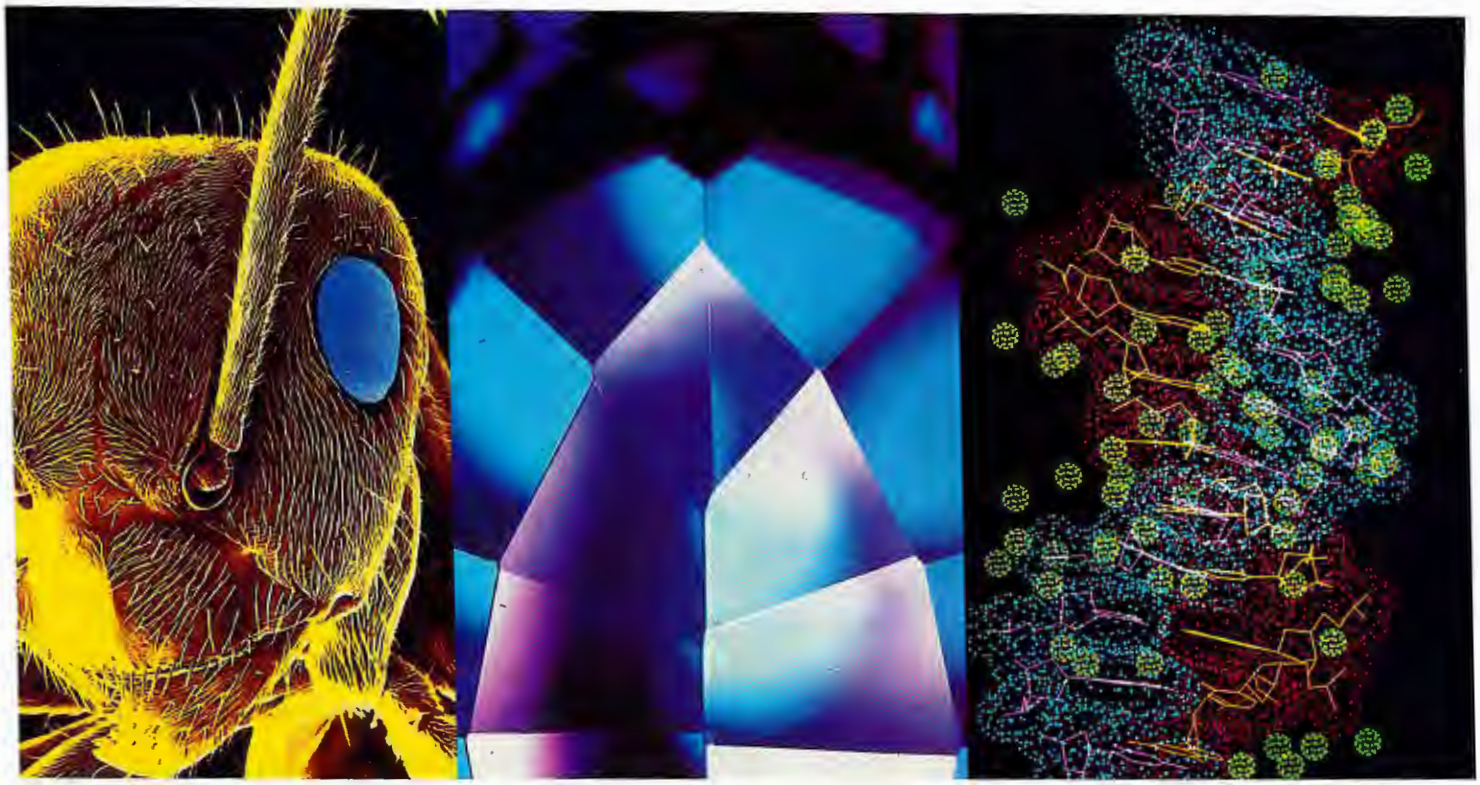

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PHYSICAL SCIENCES 106
405-744-5920

April 19, 1989
(received 4/22/89)

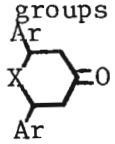
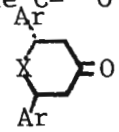
Dr. B. L. Shapiro
966 Elsinore Court
Palo Alto, CALIFORNIA 94303

Sort Title: ^{17}O Of 1-Hetera-4-cyclohexanones

Dear Barry:

Your first note arrived this week and we can happily say that we have acquired some new data on our XL-400 which is now fully operational. We have examined a large number of 1-hetera-4-cyclohexanones and relatives in bicyclic systems in an effort to determine if the ^{17}O resonance from the $C=^{17}O$ group (natural abundance) could provide any diagnostic stereochemical features in such heterocycles. Using D_3CCN/H_3CCN as the solvent system at 70°C at about 0.1 M concentration, we can acquire useful ^{17}O shifts within an hour or less in a 10 mm tube with spectrometer settings of 44,248 (spectral width), 1,024 (data points) a 40 μ pulse width, a 1ms acquistion delay, and a 0.012 sec acquisition time (this gives 1×10^5 to 4×10^6 scans). Some improvement in S/N was gained by adding 20 Hz exponential broadening factor to the FID prior to FT. Digital resolution was improved to ± 1.4 Hz by zero filling to 16 K data points prior to FT. Reproducibility of the chemical shift data is estimated to be greater than ± 1.0 ppm.

It is interesting that in the general formula shown below that we observe a deshielding of the ^{17}O in $C=^{17}O$ in going from the <u>cis</u>- to <u>trans</u>-isomer regardless of whether or not we have a flattened ring (X = S, etc.) or normal chair conformer (X = O, etc.). We are currently investigating a number of substituent effects, including those systems which have groups alpha to the $C=^{17}O$ group.

[<u>cis</u>-isomer]   [<u>trans</u>-isomer]

We trust this will serve as our contribution for the NMR Newsletter. Best regards.

Sincerely yours,

Darrell

K. Darrell Berlin
Regents Professor

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

February 28, 1989
(received 3/23/89[sic])

SOURCE OF BACKGROUND FLUORINE RESONANCES

Dear Barry,

For the past several years we have been working with cell-introducible fluorinated "indicator" molecules sensitive to various aspects of cellular metabolism which provide NMR detectable signals.[1] The approach offers the high sensitivity of fluorine and the essentially complete absence of endogenous 19F resonances. One unfortunate obstacle to such studies is the presence of a significant fluorine background, typically manifest as a rolling baseline artifact, which is frequently due to "teflon" or a related polymer present in the probe.

However, physiological studies using in-house probes showed us the same problem despite efforts to exclude background-contributing materials. Removing the probe from the magnet similarly removed the problem, showing the background problem to be an NMR phenomenon. One of the probe's connectors appeared to have a teflon lining separating the center conductor from the shield; eliminating this connector from the circuit eliminated the problem. Alternatively, the connector could be placed directly into the center of the sample volume without contributing a 19F resonance to the spectrum. An NMR experiment was presumably set up within the connector itself during an rf pulse. Although spurious background resonances from materials present in cables and connectors have doubtlessly been encountered by others, this was our first experience with it, and suggests this as a general problem about which spectroscopists should be aware.

Beware of cables bearing rf fields!

Sincerely,

Alex Funk — Alex Funk

Robert E. London — Robert E. London

[1] Levy et al., Am. J. Physiol. 252, (Cell Physiol. 21): C441-C449, 1987; Biochemistry 27, 4041-4048; 1988.

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Department of Physical Chemistry

Professor Peter Stilbs

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

March 22, 1989
(received 3/29/89)

Re: BRUKNET-VAX Ethernet data transfers and conversion for NMR1/NMR2/IMAGE

Dear Barry:

Thank you for your gentle reminder; I hope this arrives in time for the deadline. As I indicated in my previous letter I hoped to have some experience with the BRUKNET software and hardware by now.

The BRUKNET Ethernet hardware is a 19" rackmount kit that is a bit awkward to physically connect to en existing MSL console, due to cable lengths and general layout. It has Thinwire as well as Baseband Ethernet connectors. The unit (including an H-4000 and a 20m transciever cable) arrived without any hardware documentation. The software and its general operation (ver. 870701) is quite well documented on the other hand. Complete source codes (FORTRAN on the VAX side) are included, and one needs to install the appropriate version on both the VAX and the ASPECT 3000 side. This is relatively easy, although one needs VMS system privileges of all kinds on the VAX (see below). To get the unit functional required quite a lot of phone calls and FAXes to Udo Günther at Bruker in Karlsruhe; we got in all respects very knowledgeable and detailed answers and advice, however.

On the software side, the default setups worked "as received", although one does not at all need as high privileges on the VAX system as stated in the instructions; in particular one does not need the lethal BYPASS privilege. BRUKNET exchanges data ASPECT-VAX through a constantly running detached process (called BRUKNET) on the VAX (normally in state CEF; common event flag wait). It uses its own Ethernet protocol (10-10), which is unrelated to the DECnet protocols. We are still suspicious about possible interference (we have a Local Area VaxCluster with 11 nodes, including terminal servers and diskless workstations). On the VAX and the ASPECT side there are communication programs of similar appearance (called BRKCMD and BRUKNET, respectively). Data transfers can, in principle, be initiated from both sides and also between ASPECT computers on different spectrometers (provided they are equipped with the Ethernet hardware/software).

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Initially, we could not get the unit started at all. It turns out that there is internal hardware strapping; the default is Baseband - we use Thinwire, so we had to go down to the local shop an buy 9 strapping plugs. In addition, the Thinwire connector was not even soldered in to the board... Data transfers were irreproducible to begin with; error messages were totally confusing and meaningless. The first thing to find out was that the software does not properly handle *multi-file* transfer commands (initiated on the VAX side) of type "GET DATA.* " from ASPECT to VAX. Once one has issued such a command, the system is screwed up for the reminder of the session and BRUKNET needs to be restarted on both the VAX and ASPECT side. In the opposite direction ("SEND DATA.* ", issued on the ASPECT) multi-file transfer commands work without any problems.

To make a long story shorter we feel that the system works fairly well now, provided that one uses it in a strict and restricted manner: Transfers are exclusively run from the spectrometer side, never from the VAX. The detached BRUKNET process on the VAX is started by a privileged user. BRUKNET can only write in the VAX directory that was default when it was started; that directory is therefore used as a common transfer area for all users. For similar reason "the privileged user" that started BRUKNET on the VAX must have a line in his LOGIN.COM like `$set prot=(S:RWED,O:RWED,G:RW;W:RW)/default`, so that the stored files get a protection at a level so that anyone can read them. Similarly, the transfer directory must have WORLD access for READ. A self-submitting BATCH job cleans the transfer directory every night from files that are more than 4 days old; it is up to the user to store a copy away in his own directories before that time limit. That scheme works quite well.

Alex Macur of NMRi have provided us with a prototype version of a BRUKER-NMR1/-NMR2/IMAGE conversion program for the Bruknet-transferred files. It appears to work well with both one and two-dimensional data sets (including imaging data), but still handles T_1 data sets incorrectly in the present version. Also, it unneccesarily opens the source file for WRITE as well as READ, although only READ is needed (that is why we need the `...;W:RW)/default` protection given above at the present moment).

There appear to be hardware problems like poor error or packet collision handling or poor general performance of the Bruker Ethernet board; we have two indications of that: When our local thinwire network (originating from an 8-port repeater of the DEC DEMPR type) was expanded with a few more workstations (with the correct topology), BRUKNET failed to work; error messages on the ASPECT were unbelievable. After reconnecting, so that the Bruker Ethernet controller became the only unit on its Thinwire segment originating from the DEMPR, everything worked again. During the same time there were no problems whatsoever within the DECnet or LAVC communication on the same line. The second indication of poor performance is that BRUKNET hangs, and needs to be restarted on the VAX side, as soon as any one of the 11 VAX nodes is rebooted (which causes quite a lot of Ethernet traffic).

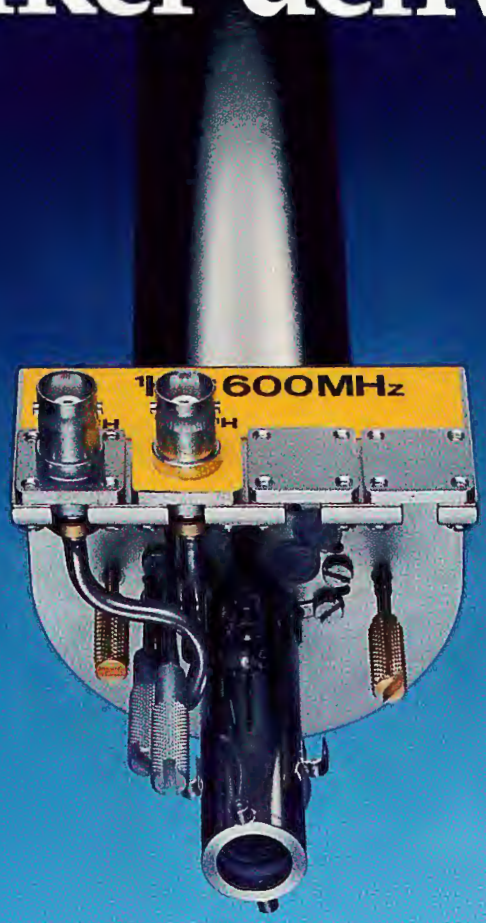
In conclusion, we find the situation acceptable, if not trouble-free. I would be glad to hear advice from other people that have experience with Bruknet-VAX transfers.

I hope that the layout and information content density of this letter is acceptable for inclusion into TAMU Newsletter.

Yours Sincerely,

Peter Stilbs

Bruker delivers.



Again.

Since its foundation in 1960, Bruker has continued to make major contributions to the field of commercial analytical instrumentation, especially NMR:
1963: World's first pulsed NMR spectrometer.
1967: World's first truly multinuclear high resolution NMR spectrometer.
1969: Introduction of Fourier transform techniques for NMR.

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Then in 1986 we introduced the first microscopy accessory for NMR.

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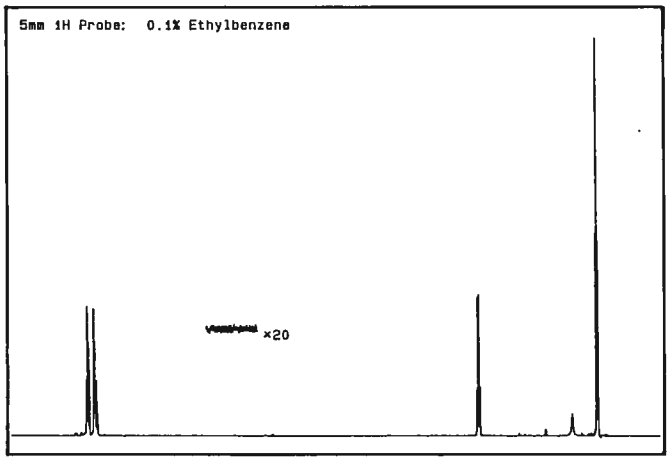
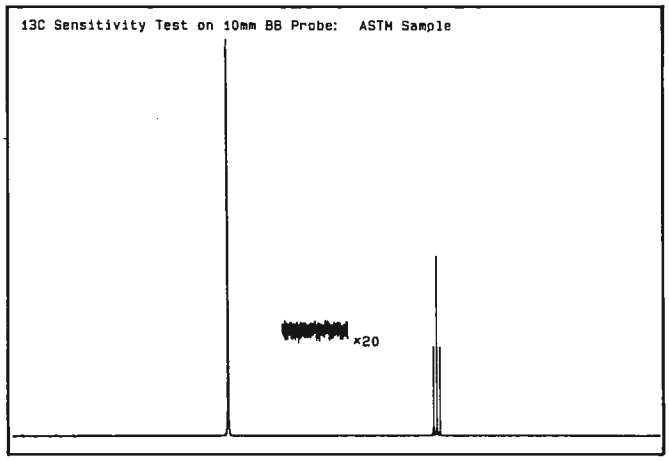
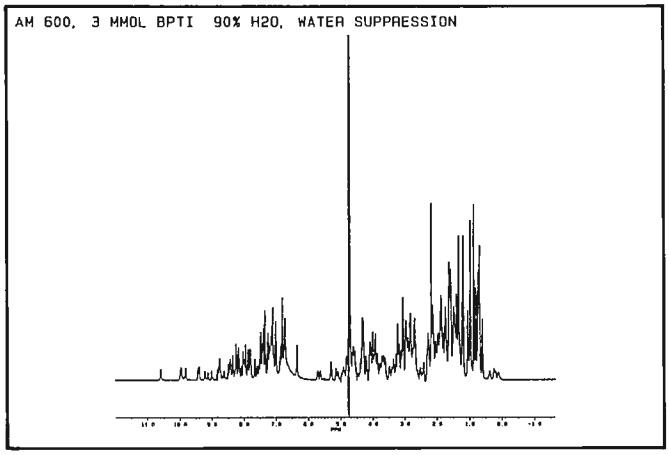
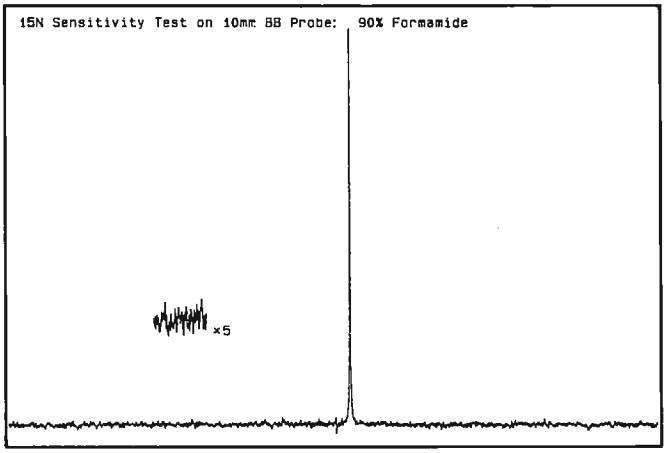
AM 600 NMR Spectra









Current AM 600 specifications (subject to change):

Probehead	Nucleus	Test	Value
^{1}H selective (5mm)	^{1}H	lineshape	10/20
		S/N	600:1
Broadband (5mm)	^{13}C	S/N (ASTM)	220:1
		S/N (10% EB)	180:1
		lineshape	6/15
	^{15}N	S/N (FORM)	25:1
Broadband (10mm)	^{13}C	S/N (ASTM)	650:1
		S/N (10% EB)	375:1
		lineshape	6/15
	^{15}N	S/N (FORM)	80:1
Resolution (all probes)			0.25 Hz

Magnet drift: ca. <40 Hz/hr

EB = ethylbenzene with ^{1}H decoupling
ASTM = 60% C_6D_6 in dioxane
FORM = Formamide (^{1}H decoupling without NOE)
LINESHAPE: ^{1}H = $CHCl_3$ linewidth at height of ^{13}C satellite/at 20% this level
^{13}C = C_6H_6 linewidth at 0.55%/0.11% of peak height

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NMR FT-IR DATA SYSTEMS BRUKER NMR IMAGING EPR MS

Tulane
Department of Chemistry
Tulane University
New Orleans, Louisiana 70118
(504) 865-5573

April 18, 1989
(received 4/19/89)

Dear Barry,

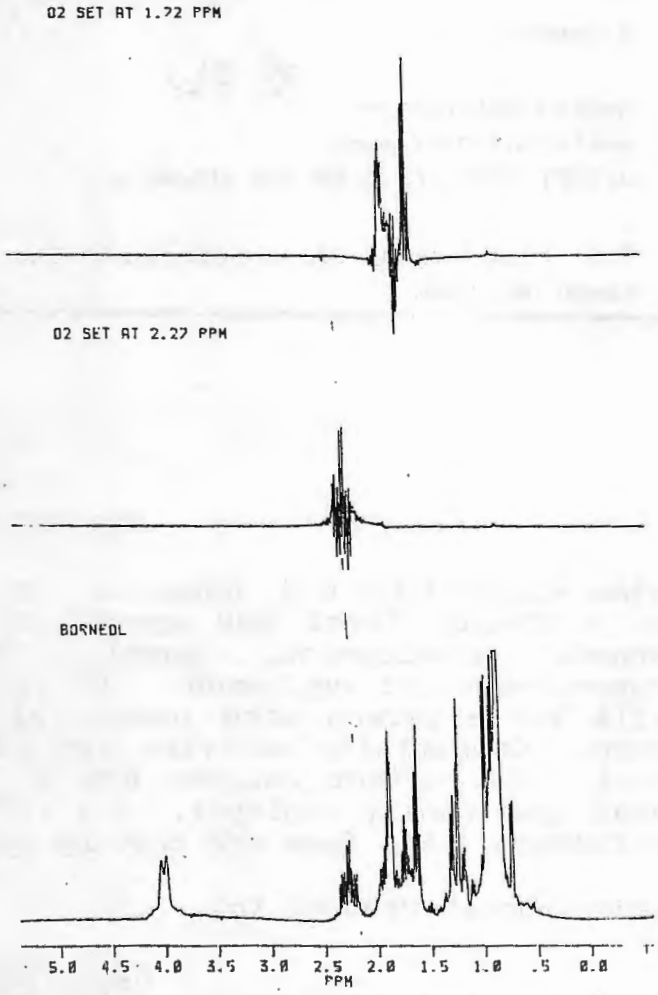
The use of Gaussian shaped pulses is quite useful due to their selectivity, but many NMR spectrometers are not equipped to produce such pulses. Gerhard Wider (now at ETH, Zurich) suggested a pulse train to simulate a Gaussian pulse, in particular for a selective COSY experiment. We have found this pulse useful, but having some pitfalls.

On our Bruker AF-200 (which has a process controller, required for this experiment) we were able to use the pulse for a selective H-C J-resolved experiment. A problem with the standard microprogram is that a mechanical relay is used to change between the required power levels at each scan. The new pulse bypasses the problem as the high level setting is used for the pulse and decoupling.

One pitfall is the DANTE sidebands from the interpulse delays at O2 ± 1/T where T is that delay (D1). Irradiation of unwanted signals is easily checked by a quick 1 pulse experiment using the selective pulse. Another limitation for us is that our decoupler and receiver are not phase locked, so effectively this "pulse" is only useful for heteronuclear experiments.

On our system we found that the 90° pulse at 55H (effectively the weakest usable power) was 3.3 msec. The total P1 value in this pulse adds up to 100, so for a 180° pulse, we used 66 usec for P1.

To demonstrate the selectivity limits of the pulse I have included the data below obtained with single pulse, one scan, experiments on borneol, setting the decoupler to two different frequencies. In both cases I set P1 to 3.3 usec, a 90° pulse at the pulse frequency. Clearly, the peak at 2.27 ppm can be selectively irradiated, while the central signal of the congested region at 1.72 ppm cannot be.



One advantage of this type of pulse is that one can arbitrarily shape the pulse by changing the values used for each fractional pulse, but computer hardware will limit the total number of individual pulses used in any particular experiment.

The "pulse" sequence is:

(P1*.125 PH1 D2 P1*.203 PH1 D2 P1*.319 PH1 D2 P1*.486 PH1 D2):D (P1*.719 PH1 D2 P1*1.03 PH1 D2 P1*1.43 PH1 D2 P1*1.92 PH1 D2):D (P1*2.51 PH1 D2 P1*3.17 PH1 D2 P1*3.89 PH1 D2 P1*4.62 PH1 D2):D (P1*5.31 PH1 D2 P1*5.93 PH1 D2 P1*6.41 PH1 D2 P1*6.72 PH1 D2):D (P1*6.82 PH1 D2 P1*6.72 PH1 D2 P1*6.41 PH1 D2 P1*5.92 PH1 D2):D (P1*5.31 PH1 D2 P1*4.62 PH1 D2 P1*3.89 PH1 D2 P1*3.17 PH1 D2):D (P1*2.51 PH1 D2 P1*1.92 PH1 D2 P1*1.43 PH1 D2 P1*1.03 PH1 D2):D (P1*.719 PH1 D2 P1*.486 PH1 D2 P1*.319 PH1 D2 P1*.203 PH1 D2):D (P1*.125 PH1):D

A slice of the data obtained from the long-range J-resolved experiment is shown in Fig. 2.

Sincerely,

Andrew Waterhouse
Assistant Professor
BITNET: CMØAACF @ VM.TCS.TULANE.EDU

P.S. I am looking for a used synthesizer for the range 50-80MHz.

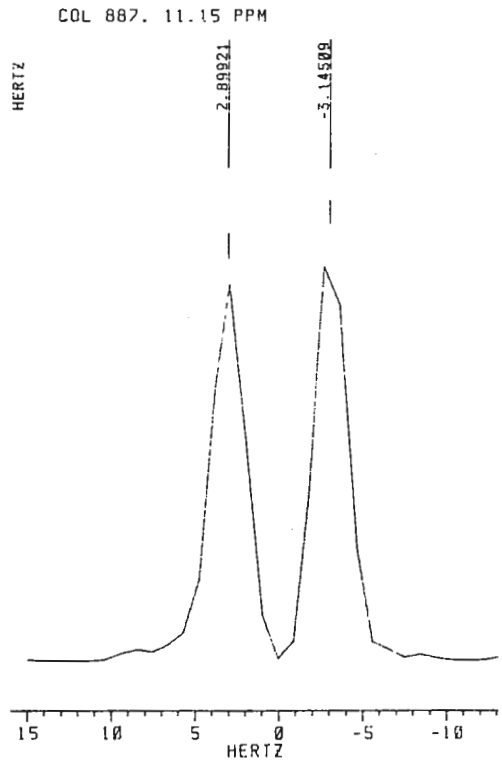


Figure 2

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Villeurbanne, March 16, 1989
(received 3/29/89)

Dr B.L. SHAPIRO
TAMU NMR News Letters
966 Elsinore Court
PALO ALTO CA 94303 (USA)

SERIAL FILE TRANSFER FROM A 3000 TO HP 9000

Dear Dr Shapiro,

We want to describe the connection realized in our laboratory, between A3000 and HP9000 (330 series). Data, spectra or images are transferred from a CXP spectrometer to the HP computer via a RS 232 cable - The serial port C of A3000 is used and the protocol is as it follows :

1) Conversion of FILE.001 in a ASCII file FILE.ASC using a Fortran program (called CXP) written in the A3000.

(2) Transmission using the Bruker command
LIST FILE.ASC/=CO (the HP 9000 is considered as a printer).

3) Reception using a Basic program (called RS 232) stored in the HP 9000 and activated before transmission starts.

4) The program "RS 232" performs the ASCII to binary conversion and creates binary files.

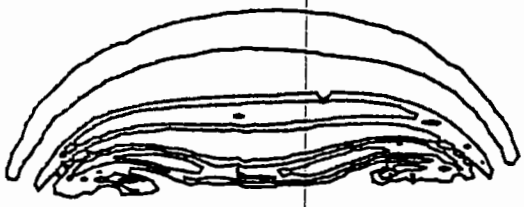
Finally array data [DIM (SI,NE)] are available on floppy disks for further processing. Moreover we have written several routines in order to draw data and spectra or to display images on a digital plotter. Figure 1a shows the spatial response of a stimulated echoes sequence with surface coil and Figure 1b exhibits the corresponding isointensity curves obtained using the HP contour plot routine.

Please credit this letter to Professor J. DELMAU as a renewal contribution.

Yours sincerely

Pierre PIMMEL Hana LAHRECH Danielle GRAVERON André BRIGUET

(a)



(b)

Figure 1 :

Spatial response of stimulated echo sequence using surface coil is given by a $\theta \sin^3\theta$ law.

a) 128 x 128 image of a planar phantom displayed on a Bruker system

b) Corresponding contour plot on H.P.7475A

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

Nijmegen, 28-03-1989.
(received 4/6/89)

Magic Angle Spinning of viscous liquids.

Dear Dr. Shapiro

The tasks of the Dutch National HF-NMR facility at the University of Nijmegen have recently been extended with solid state NMR. The Bruker AM 500 of the facility has therefore been provided with a solid state accessory. This accessory comes with a Bruker MAS probe equipped with a 7 mm double air bearing spinner assembly.

Although we are supposed to do solid state NMR, we are occasionally confronted with samples whose physical appearance is far from solid. This is because MAS spectra of viscous liquids are often more resolved than spectra taken under conventional high-resolution conditions. This is generally true when molecular motions in the sample become restricted, i.e. the molecules can no longer use all degrees of freedom.

In general, performing MAS experiments on (viscous) liquids is a hazard for the probe (and to some of our users mental condition), because the liquid is spun out of the rotor and is smeared all over the stator.

We have found a very easy trick to overcome these problems; after the spinner has been filled, a piece of Teflon thread seal tape is stretched over the spinner opening. Then the (Kel-F) rotor cap is pushed into the spinner. This results in a very thight fit of the cap. The excess of Teflon tape coming out of the rotor must be cut of very carefully with a scalpel knife. It may be necessary to fill up the little hole in the Kel-F cap e.g. with paraffin. We have used this procedure on liquids with varying viscosity and got excellent results. The solutions stay in the rotor and spinning speeds up to 1.5 kHz are easily attained. We hope that this little trick will help other spectroscopists with their MAS experiments on liquids.

Sincerely Yours,

G. Nachtegaal A.P.M. Kentgens

Please credit this contribution to the account of Prof. E. de Boer.

SHEMYAKIN INSTITUTE OF BIOORGANIC CHEMISTRY USSR ACADEMY OF SCIENCES

PROF. V.F. BYSTROV

Ul. Miklukho-Maklaya, 16/10
117871 GSP-7 Moscow V-437
USSR

Tel. 330-56-38
Telex 411982 trem su
Cable Bioorganika

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

April 3, 1989
(received 4/8/89)

Title: Spurious Frequencies in Modified WM-500 Bruker and Their Removal

Dear Barry,

Our eight year old WM-500 Bruker recently was modified by AM-type Transmitters f_1 and f_2. When running spectra several shortcomings were revealed: 1) artefacts in 1D spectra, 2) influence of decoupler setting on S/N, 3) "grid-like" noise pattern in 2D spectra. For instance, the S/N in homo-decoupling mode (f_2 out of signal region) is decreased by 65% when the output power is increased from 63L to OL.

The reason is direct pickup by the Receiver signals from the Transmitter f_2 and the frequency Tripler 166.67 MHz of the H-H Decoupler. To decrease the level of pickup from the Tripler we put a duct capacitor 4700 pF in the T1 collector power line.

For leveling out the spurious pickup generated by Transmitter f_2 we incorporated the PIN diode SPDT switch (Mini-Circuits PSW 1211) in between the Aspect 3000 computer O2 output and the Transmitter f_2 O2 input. The Switch is under control of the same pulse generator as the Transmitter f_2.

As a result: 1) S/N became 250:1 (it was 160:1 before), 2) when decoupler power is increased from 63L to OL the S/N falls only on 14%, 3) grid-like pattern disappears.

With best regards,

Vladimir

Sincerely yours,

A. Gurevich

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			10 g	14.
			5 x 10 g	69.
			10 x 10 g	135.
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			10 g	22.
			5 x 10 g	100.
82-84077	Benzene-d_6	99.6	10 x 1 g	18.
			10 g	18.
			5 x 10 g	75.
			10 x 10 g	145.
82-80556	Chloroform-d	99.8	100 g	18.
			5 x 100 g	80.
			10 x 100 g	142.
			1 kg	135.

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			5 x 100 g	215.
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			25 kg	8500.
			50 kg	16250.
82-70002	Deuterium Oxide "100%"	99.96	10 g	15.
			5 x 10 g	50.
84-70001	Deuterium-depleted Water	$< 5 \times 10^{-5}$	25 g	25.
			4 x 25 g	90.
			10 x 25 g	200.
			20 x 25 g	300.
			30 x 25 g	400.
			1 kg	500.
82-00807	Dimethyl-d_6 Sulfoxide	99.9	10 x 1 g	12.
			10 g	12.
			5 x 10 g	56.
			10 x 10 g	110.
82-00809	Dimethyl-d_6 Sulfoxide (multi-dose septum vials)	99.9	10 g	12.
			5 x 10 g	56.
			10 x 10 g	110.
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			10 g	43.
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April 14, 1989
(received 4/19/89)

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

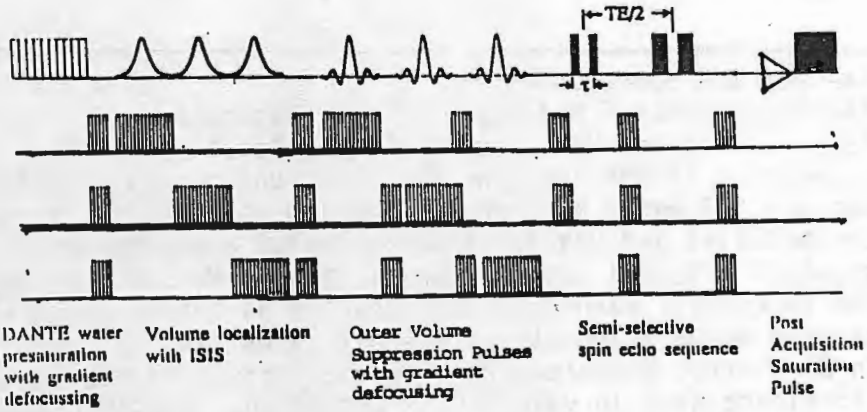
RE: ^{1}H NMR Spectra of Human Brain

Dear Dr. Shapiro:

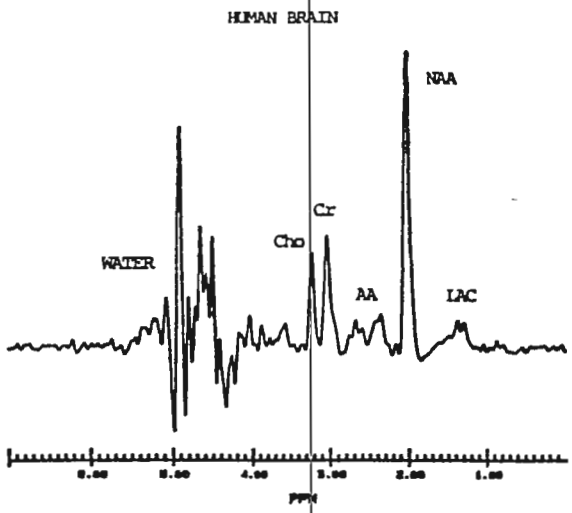
For the past two years we have been performing image localized NMR Spectroscopy on human organs using a 2.0T Philips MRI/MRS System. Several other investigators have reported water-suppressed ^{1}H NMR spectra of human brain using stimulated echoes. A problem with this approach is a 50% loss of S/N due to the stimulated echo and a further loss of S/N due to J-modulation.

Recently, Dr. Hoby Hetherington in this laboratory implemented a modified ISIS technique for ^{1}H NMR using homogeneous coils; thus image-selected ^{1}H NMR spectra can be obtained from any region of the brain without the S/N losses associated with stimulated echoes. The pulse sequence is shown below:

MODIFIED ISIS SEQUENCE



The pulse sequence, minimizes lipid subtraction errors by saturating parallel slices outside the VOI with sinc-cos pulses and dephasing gradients. Further localization is achieved using an ISIS sequence with B_1 insensitive hyperbolic secant pulses and a post acquisition saturation pulse (PASP). Water suppression is achieved using 1-1 pulses, (optimum 1.9 ppm), DANTE presaturation and gradient pulses. Data was acquired from the brains of normal volunteers (TR=3s, TE=100ms).



The outer volume suppression pulses reduced the lipid signal by a factor of 10, minimizing possible subtraction errors. In contrast to STE, ISIS allows semi-selective pulses to be used for both the excitation and refocusing pulses. When combined with a DANTE saturation pulse, the water was reduced by 10^3 to 10^5 for TE's of 20-100 ms. A typical spectrum acquired from a 100cc volume of white matter in the parietal lobe (TE=100ms) using 64 scans, (3.2 min.) is shown. The excellent localization afforded by the modified ISIS sequence detected normal brain lactate, identified by its chemical shift and 7.4 hz coupling constant.

In addition to this work, Albert Thomas is implementing a ^{1}H double quantum filter for our whole-body system. We are applying these techniques to study the effects of various brain diseases on human metabolism.

Sincerely,

MICHAEL W. WEINER, M.D.
Associate Professor of Medicine and Radiology

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The course will be a mix of theory and applications, with the understanding that it is not necessary to fully comprehend the theory in order to be able to appreciate its applications. Besides lectures, there will be ample opportunity to discuss course subjects and real-case problems brought in by attendees. There will also be a visit to the National SON NMR facility at the University of Nijmegen.

Topics to be covered:
- Basic spin interactions and solid state NMR techniques: high-power homo- and heteronuclear decoupling, magic angle spinning, cross-polarization, quadrupole NMR and two-dimensional NMR.
- Application to organic materials: characterization, molecular motions and aligment effects in polymers.
- Application to inorganic materials: organometallic complexes and silicates.
- NMR imaging of materials: the study of absorbed fluids in materials.

Who should attend:
The course is meant for those who are either involved with NMR directly and who want or need to know more about solid state NMR or for reseachers in the field of materials who want to obtain insight in the possibilities of solid state NMR. For this last group it would be helpful if they have a basic understanding of pulse NMR of solutions, for instance at the level of the textbook "Pulse and Fourier Transform NMR" by T.C. Farrar and E.D. Becker, Academic Press 1971.

Course leader and lecturers:
Prof. Dr Ir Wiebren S. Veeman (Course leader) studied Technical Physics in Delft (1967) and obtained a Ph.D. degree in Physics in 1972. After a postdoctoral stay at the IBM research Laboratory in San Jose, U.S.A., he has since been employed by the University of Nijmegen, currently as a Professor in Physical Chemistry.
Prof. Dr Hans W. Spiess has been Professor in Macromolecular Chemistry in Mainz and Bayreuth. Presently he is director of the Max-Planck Institut for Polymer Forschung in Mainz.
Dr Arno P.M. Kentgens studied Chemistry in Nijmegen where he obtained (cum laude) the drs degree in 1983. A Ph.D. degree was earned in 1987 with a thesis about several aspects of solid state NMR. After a short period in the Philips Research Laboratory in Eindhoven he is now the manager of the National SON Solid State NMR facility in Nijmegen.
Dr Alex de Groot studied at the University of Amsterdam and finished with a drs degree in Chemistry in 1981. He obtained a Ph.D. degree in Biophysics in Leiden in 1985 and has since been employed by Shell, Amsterdam. There he was directly involved in the application of NMR imaging to materials research. Currently, he is group leader of the NMR Group of the analytical section of Koninklijke/Shell Laboratory, Amsterdam

Dates/Venue: June 14-16, 1989 / Hotel Valmonte, Nijmegen, The Netherlands.
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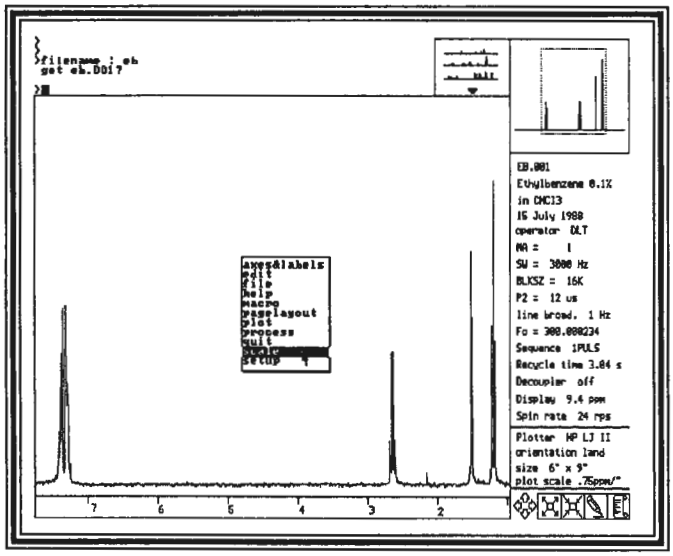

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"Shimming"

One operator adjustable parameter which has an immense influence on the quality of NMR data obtained is the adjustment of the field homogeneity. This process is commonly referred to as "shimming". The name derives from the process used for adjusting the homogeneity in large electromagnets. Back in the "good ole days" the field homogeneity was adjusted with a wrench to physically move the magnet pole faces as parallel as possible. This adjustment was the equivalent of the supercon Z or the electromagnet Y. The wrench adjustment was supplemented by adding small thin objects at strategic locations between the magnet coil and the magnet pole faces. These thin objects provided a method of adjusting the pole face gaps with higher order corrections. The thin objects were called "shims". Adding, subtracting and moving of these "shims" acquired the name shimming.

Today most NMR spectrometers use superconducting magnets and the homogeneity is adjusted with small coils of specific geometry fed by carefully regulated power supplies. Each coil is designed to have a specific field correction. These coils have the major field correcting capability "resembling" the shim name; i.e., Z^1, Z^2, Z^3, Z^4, Z^5, X, Y, ZX, ZY, XY, X^2-Y^2, Z^2X, Z^2Y, ZXY, $Z(X^2-Y^2)$, X^3 and Y^3. These coils never generate "pure" field corrections even when they are perfectly constructed. Each shim generates an "impure" correction field. Intrinsic in the design of these shim coils is a geometrical relationship by which each shim generates impurities with a specific relationship to the desired gradient, such as, Z and X impurity in a ZX shim. There are many different designs of the shim coils; but from the users point of view, the shim design with the least impurities (therefore the least interactions) is the most desirable. If all the shims did not interact to some degree, shimming would be a simple adjustment of the shim controls to maximize the lock signal. The minimum interaction shim set produces the easiest shimming process. The ease of shim adjustment translates to a higher quality of NMR data and more sample throughput. Judging by a non scientific approach (feel) and a scientific approach (field plotting and regression analysis) on a necessarily limited number of instruments, the Bruker shim sets were the easiest to shim.

The NMR operator can save a lot of potentially wasted time by getting some sample related areas under control before starting the shimming process. Some of these areas have a tremendous influence on the resolution and lineshape which obtained, as much or more than the shim controls themselves. For best results, give some attention to the following areas:

- Use a good thin wall NMR tube to maximize the filling factor and minimize the spinning sideband. The thinner the tube wall the more sample will be in the receiver coil; therefore, the better the sensitivity. An irregular tube can "bounce in the probe and generate spinning sidebands. Irregular tubes can also modulate the probe tuning and induce RF spinning sidebands. RF spinning sidebands differ from normal spinning sidebands by the fact that they are of a different phase than the main NMR signal. The higher the tube precision, the less the spinning sample will modulate the probe tuning. RF spinning sidebands are more prevalent in today's high sensitivity (i.e., high Q) probes.
- The sample should be in the probe to a depth such that the bottom of the sample is more than half the receiver coil length below the receiver coil. The sample depth needs to be more than twice the receiver coil length. Both of these conditions are due to the magnetic susceptibility changes at the ends of the solvent. Most solvents used in NMR have a larger magnetic susceptibility than the materials of which the probes are constructed. These "end effects" are difficult to shim away and are particularly damaging to low order lineshape.
- The sample should be free of particulate matter. Many samples when examined with a magnifying glass contain solid particles. Solid particles have a different magnetic susceptibility than the surrounding solution, which can reduce the field homogeneity. Further interference is generated as the particles move in a spinning sample. In bad cases, the particles are magnetic. Examine the tube in a magnifying glass between the poles of a small magnet. If when the tube is moved from one pole to another, the particles jump from one side of the glass to another, there is a problem. Having either magnetic or non-magnetic particles in the sample is a very common occurrence. Check your sample with a magnifying glass!!
- The sample and probe temperature should be equilibrated and controlled. Temperature gradients in the sample decrease the homogeneity. This is particularly true when using proton decoupling. The decoupling power must be controlled to a level which minimizes the generation of temperature gradients inside the sample. The problem is worse in water samples, in large tubes, and when the decoupling power is gated on and off during an experiment.

In the next Instrumentation Note, as the shimming process is explored further, some instrumental areas that need to be determined and controlled before the shimming process starts will be discussed.

NAVAL RESEARCH LABORATORY
WASHINGTON, D.C., 20375-5000

April 11,1989
(received 4/17/89)

Dear Barry:

MEASURING TRANSLATIONAL DISPLACEMENT PROBABILITIES

Recently we have been rediscovering bounded diffusion as a way of extending our materials imaging studies to smaller dimensions. Many samples contain compartments of fluids for which the distribution of compartment diameters is of interest, but not the spatial location of each compartment. One approach to measuring this distribution is to study the interruption of molecular diffusion caused by the compartments walls. Stejskal and Tanner [1] and others [2] have demonstrated that the pulsed gradient spin echo experiment allows this effect to be observed. Though this is an old technique, it has never gained wide popularity because of experimental difficulties and a relatively complicated analysis. We have slightly modified this experiment such that it is less error prone and the analysis more friendly.

The experiment, a constant time pulsed gradient stimulated echo, is outlined in figure 1. The problems of generating two identical gradient pulses are eliminated by switching the gradients while the magnetization is along the static field, and allowing the gradient to stabilize prior to rotating the magnetization into the transverse plane. To avoid offset problems associated with the strong gradients (1.06T/m), intense pulses (90°=2.5 μ) and a short sample (0.4cm along the gradient direction) are used. Phase cycling eliminates residual transverse magnetization and T_1 effects.

The constant time experiment allows us to map out directly the probability of translational magnetization displacement, which for these samples where spin diffusion may be ignored is equivalent to the probability of translational molecular displacement. The echo intensity as a function of gradient strength is

$$S(g) = \int \rho(r_o) \int P(r_o \mid r,t_d) \exp[i\gamma\delta g\cdot(r- r_o)]\, dr\, dr_o$$

where $\rho(r_o)$ is the initial concentration as a function of the initial position, r_o, and $P(r_o \mid r,t_d)$ is the probability that a spin initially at r_o will move to r within a time t_d. S(g) may be Fourier transformed relative to $\gamma\delta g$ (units cm^{-1}, and conjugate units cm). The Fourier transformation of the exponential approaches a delta function at $x=r-r_o$, yielding

$$I(x)=\int \rho(r_o)\, P(r_o \mid (r_o+x),t_d)\, dr_o.$$

I(x) is simply the convolution of the initial spin concentration and the probability of displacement by x. For free diffusion the initial concentration and $P(r_o|(r_o+x),t_d)$ may both be assumed to be independent of r_o, and I(x) maps out the probability of molecular displacement (Gaussian) along the gradient direction. This is shown in figure 2 for water. The self-diffusion coefficient is easily obtained from the "linewidth" of I(x).

For bounded diffusion confined to a container of perfectly reflecting walls, I(x) is the auto-correlation function of the compartment's shape along the gradient direction. In this case the compartment width may be read directly as half of the extent of I(x) (displacements from +l to -l are allowed in a container of width l). This is shown for yeast cells in figure 3.

By following the temporal development of I(x) for various times t_d, the different mechanisms of translational displacements may be identified: the Gaussian response of free diffusion broadens as the square-root of time; for bounded diffusion I(x) remains constant for times larger than the mean diffusion time across the compartment; permeable membranes yield a response which is a combination of these two; and for wall relaxation transverse spin magnetization is destroyed for large displacements.

By this technique it is possible to distinguish among various diffusional processes, and to measure diffusion coefficients and critical dimensions in a straightforward manner. The signal from each compartment adds coherently resulting in a large S/N gain which in turn allows for very large gradients and high resolution (0.1μ).

David Al

D.G. Cory A.N. Garroway

Code 6122, Chemistry Division

Pulsed Gradient Stimulated Echo

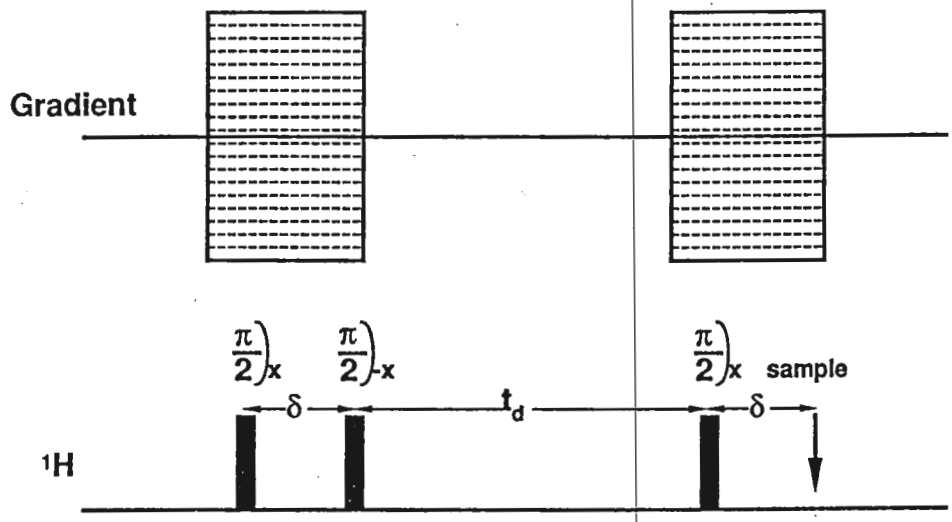


Fig. 1

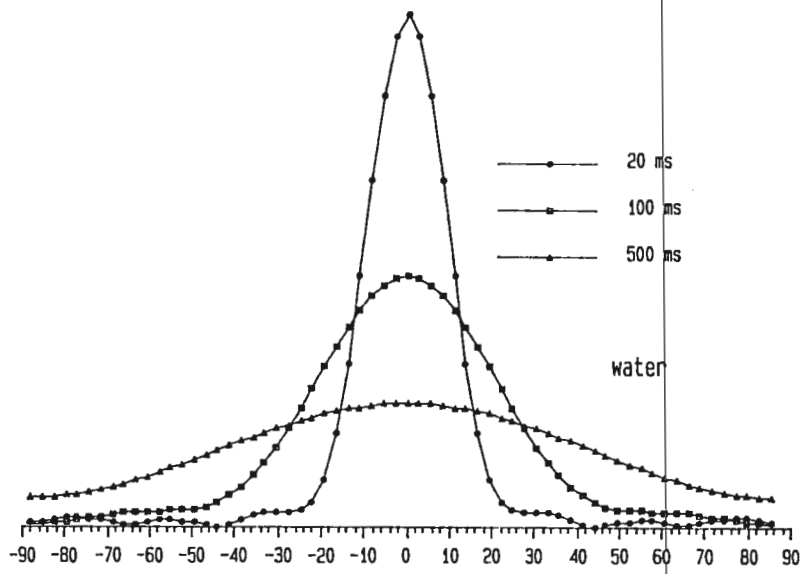
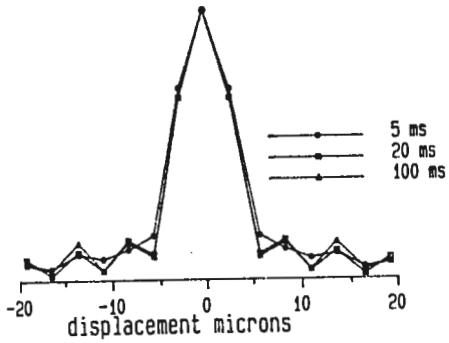


Fig. 2



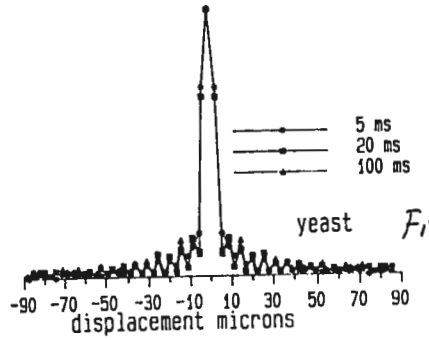


Fig. 3

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

31 March 1989
(received 4/15/89)

Dear Dr Shapiro,

PARSNIPs and Proteins

At the Frythe, we have developed a program for simulating the partial proton nmr spectrum of a protein, based on the ring current shifts of several aromatic and aliphatic amino acids, derived from X-ray crystal structure co-ordinates, and also for predicting interresidue noe's for the same amino acids. True to form for nmr spectroscopists, this program was quickly dubbed PARSNIP (Program for Analysing Ring current Shifts and NOE's In Proteins) (1).

Recently we have used this routine to help us make several key assignments in the proton nmr spectrum of cardiac troponin C (cTnC). cTnC is one of a family of highly homologous calcium-binding proteins (e.g. calmodulin CaM and skeletal troponin C sTnC). It has Mr≈18,000, which on our elderly AM360, makes it "large" on the nmr scale (but not necessarily on the biochemical scale). The rigorous sequence-specific assignment procedure, based on COSY and NOESY, was therefore largely ruled out, and we have relied instead on a combination of nmr experiments plus PARSNIP to give us some clues for assignment.

No x-ray crystal structure co-ordinates are available for cTnC at present; however, the structures of CaM and sTnC are available. We mutated the CaM structure to obtain a working model for cTnC, using bits of the sTnC structure where appropriate (e.g. the N-terminal helix, absent in CaM, but present in sTnC and cTnC). After a period of molecular mechanics with the package AMBER (2), we obtained a reasonable working model of cTnC.

In Figure 1, the PARSNIP simulated partial spectrum is shown compared with the experimentally observed proton nmr spectrum. Some of the assignments are marked in on the simulated spectrum. Overall, there is a good match of the predicted and observed profiles of the aliphatic and aromatic regions, and also with respect to the upfield and downfield shifted resonances in both regions.

Using these clues as a starting point, we combined them with Ca2+ titration, COSY and 1-D and 2-D NOE data, plus the NOE prediction routine of PARSNIP, to make assignments for all Phe residues (Tyr residues were assigned previously (3)). We also assigned some Met, Leu and Ile, and some Hα proton resonances. These are shown in Figure 2. Interestingly, the only incompatible prediction of the PARSNIP program is for $V28Y_1$. This residue is in a region of extensive mutation and insertion, in what was a Ca2+ binding loop in CaM, but no longer retains this function in cTnC. The chemical shift of this amino acid would seem to be a result of some anomalous geometry in this region.

Nevertheless, we are confident of having constructed a useful working model for cTnC, obtained a consistent set of assignments, and are currently using these to clarify some drug-binding studies. This work is soon to be published. We hope this contribution will stave off some pink and green ultimatums on Dave Reid's subscription.

Best wishes,

L MacLachlan

Lesley MacLachlan

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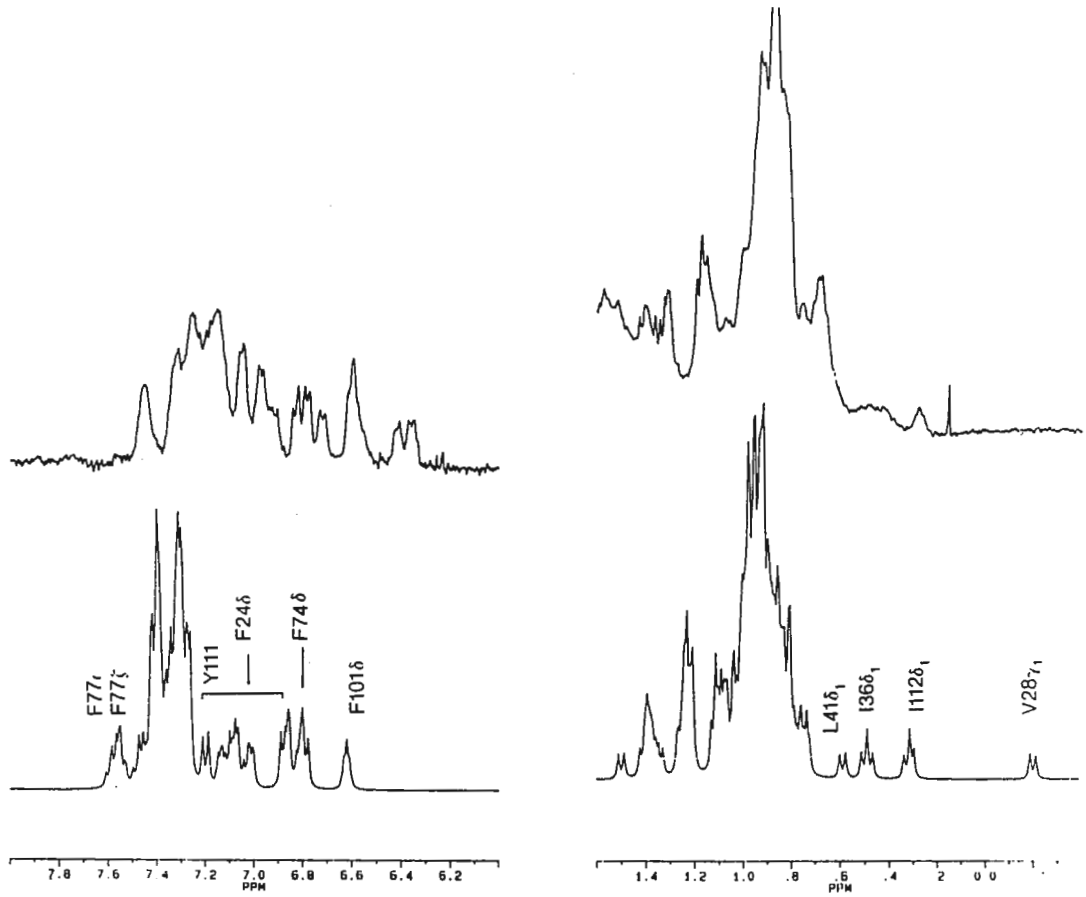


Figure 1: PARSNIP (lower) and experimental (upper) spectra.

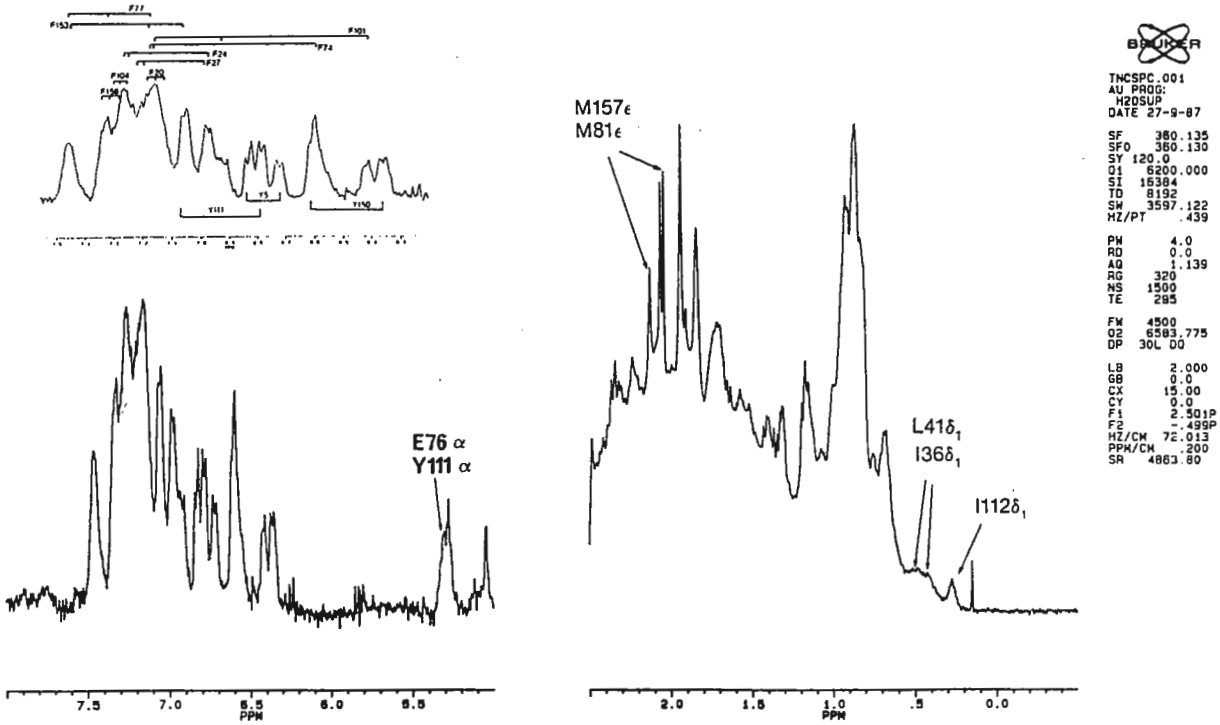
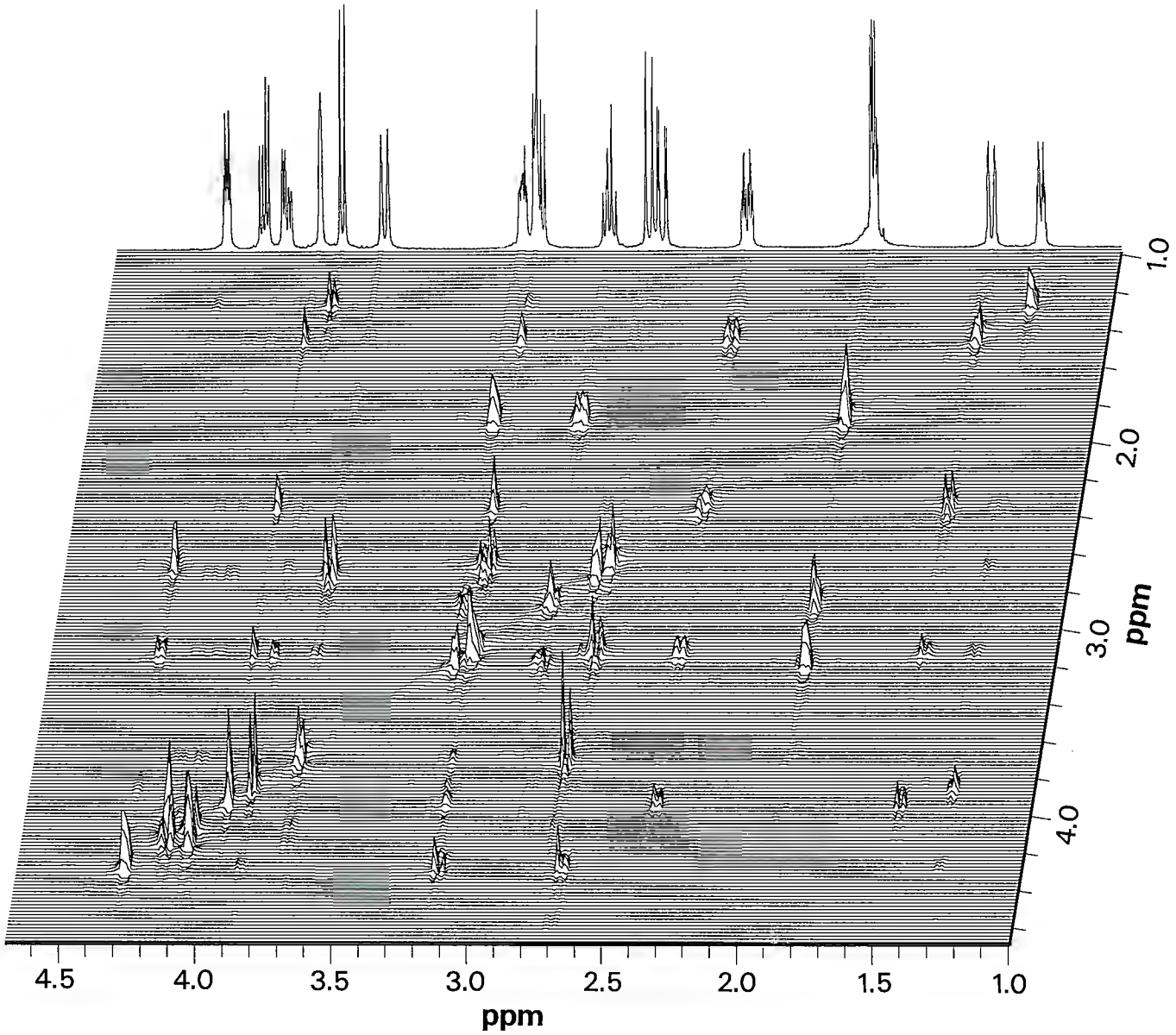


Figure 2: Assignments in the 'H-NMR Spectrum of cTnC.



HOHAHA of Strychnine on an Omega 600

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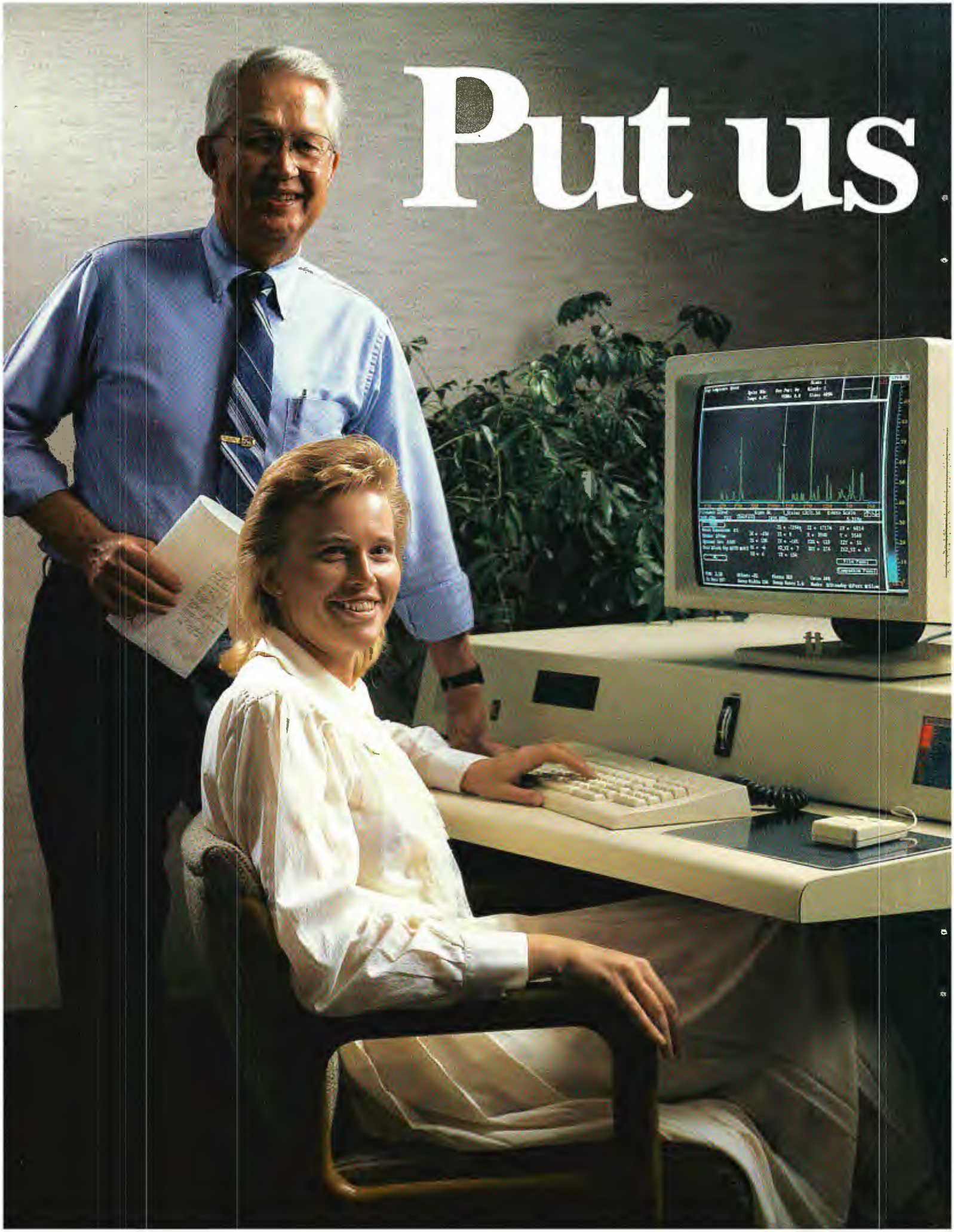
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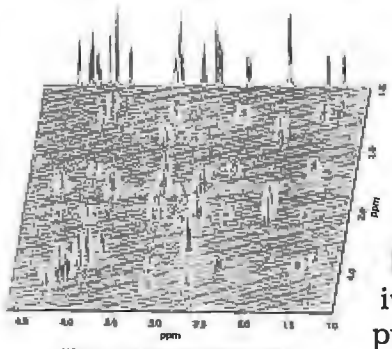

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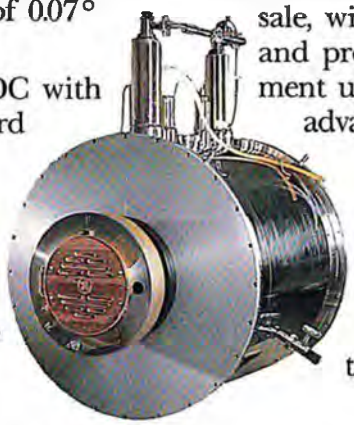

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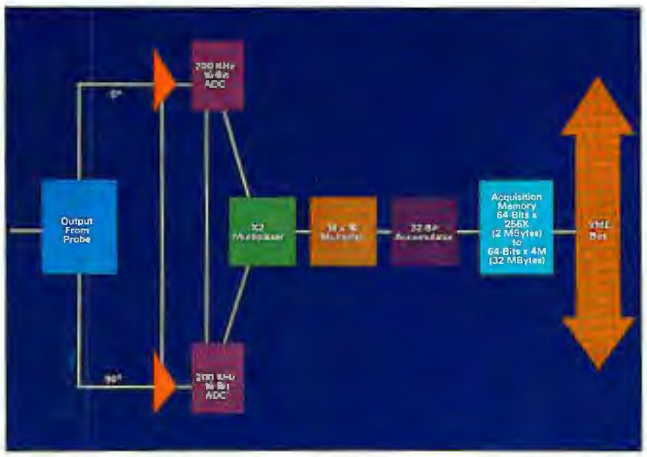

Fig. 1

The Alpha HDR digitizer.

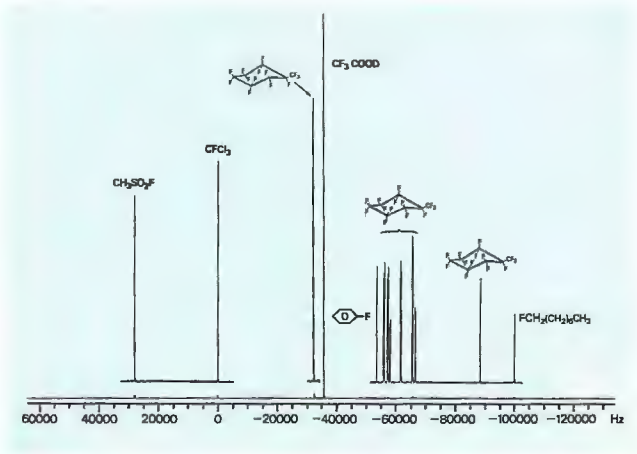

Fig. 2

200 KHz spectral width ^{19}F spectrum acquired on a GN-500 Omega System. Note the extremely flat baseline obtained with the Alpha HDR.

GE NMR Instruments

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To: Professor Bernard L. Shapiro
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March 7, 1989
(received 3/30/89)

Jumping Spins cause Jumpy Fields.

A Fundamental NMR Tribute to Cor MacLean.

Dear Dr. Shapiro,

I like to present this contribution at the occasion of the recent retirement (February 1989) of Cor MacLean as Professor of Physical Chemistry at the Vrije Universiteit Amsterdam. The fundamental NMR work of Prof. Maclean and his cooperators has always been well received by the NMR community. The main topic of his research interest is the study of oriented molecules under the influence of external forces, such as electric and magnetic fields or in liquid crystals. A good survey of the work performed by his group can be found in three review papers (1-3).

Working myself on Biomedical NMR applications, I recently encountered the manifestation of a fundamental property of Nuclear Magnetic Resonance. The title stands for the observation that the longitudinal nuclear magnetization contributes to the magnetic resonance field.
In the infancy of NMR, Dickinson (4) considered the possible contribution of the nuclear magnetization to the magnetic field. He concluded that it could be ignored, an assumption that has persisted to the present day.
Many methods for the detection of the ^1H signal of lactate in tissue have been published. An attractive one to me and my collegues Peter Huijing, Koert Zuurbier and Jaap Bulthuis was the editing method proposed by Williams et al. (5), where the water is suppressed and the lactate methyl signal is obtained by a spin-echo difference measurement using the pair of pulse sequences:

1331 - 1/2J - 2662 -1/2J - AQ [a]
and 1331 - 1/2J - 180 -1/2J - AQ [b].

I tested the 2 sequences separately using both D_2O and H_2O as solvent, without field-frequency lock. The result was puzzling at first sight (Fig. 1). Seq. [b] in H_2O consistently deviated in phase by some 30°, all measuring conditions being the same. Further investigation showed that the same phase shift occured for all resonances in the sample. Realizing that the only difference between the experiments involves the nuclear species of the solvent, we convinced ourselves that we were observing a change in magnetic field in the second halve of Seq. [b] due to inversion of the nuclear water magnetization! A calculation shows that the inversion of 100 M of protons in a superconducting magnet causes a change in the magnetic field of about -0.0025 ppm due to the bulk volume nuclear susceptibility; this quantitatively agrees with the observed phase shift.
The effects of the change in magnetic field after an *rf* pulse can show up in many ways, in particular at high magnetic fields in samples containing large amounts of protons. A unique feature is its transient nature, as spin-lattice relaxation and the lock system try to restore the equilibrium magnetic field during the acquisition of the FID. Fig. 2 shows the lineshape of the acetone resonance when the H_2O resonance is rotated independently. In spin-echo experiments, both signal phase, shape and position will depend on the echo distance. In the above experiment , Seq. [b], phase shifts up to 1000° have been observed. In 2D experiments the longitudinal magnetization varies widely as a function of t_1, and a contribution to t_1 noise results. A preliminary, extreme example is shown in fig. 3.

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4. W.C. Dickinson, Phys. Rev. **81**, 717 (1951).
5. S.R. Williams, D.G. Gadian & E. Proctor, J. Magn. Reson. **66**, 562 (1986).

Finally, would you please forward the next issues of the Newsletter to: Dr. J. Bulthuis, Department of Physical and Theoretical Chemistry, Faculty of Chemistry, Vrije Universiteit, Boelelaan 1083, 1081 HV Amsterdam, The Netherlands.

Dr. Hommo T. Edzes, Coordinator Biomedical NMR Research

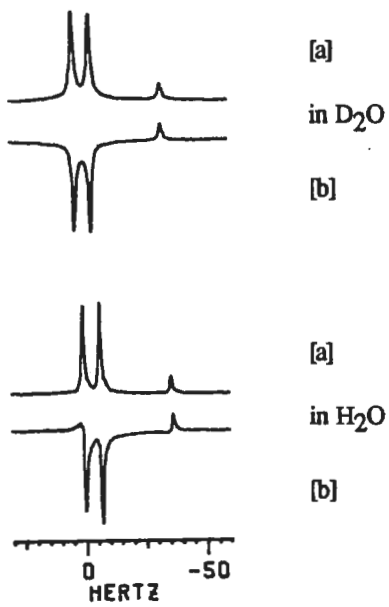

Fig. 1. Lactate selection in D_2O and H_2O at 400 MHz using pulse sequences [a] and [b] at 400 MHz. 1/2J=34 ms. The additional peak is of t-butanol. Note the overall phase shift in the lower spectrum [b].

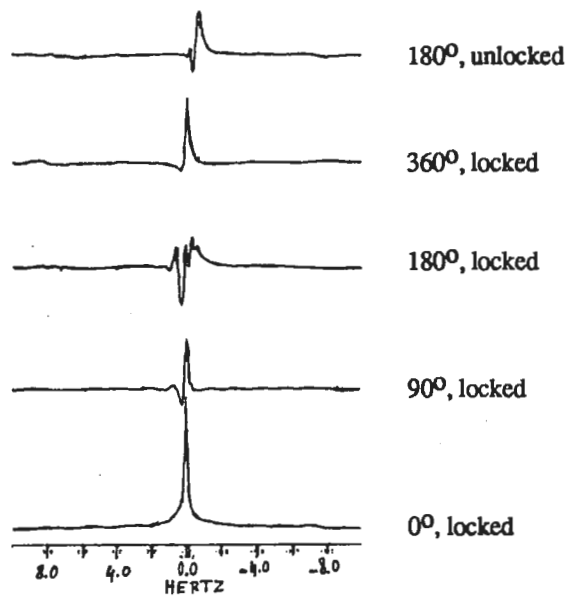

Fig. 2. Lineshape of 1% acetone in 90% H_2O and 9% acetone-d_6. Water and acetone magnetizations are rotated separately using $1\bar{1}$ and 11 pulses. The rotation of the water magnetization is given in °.

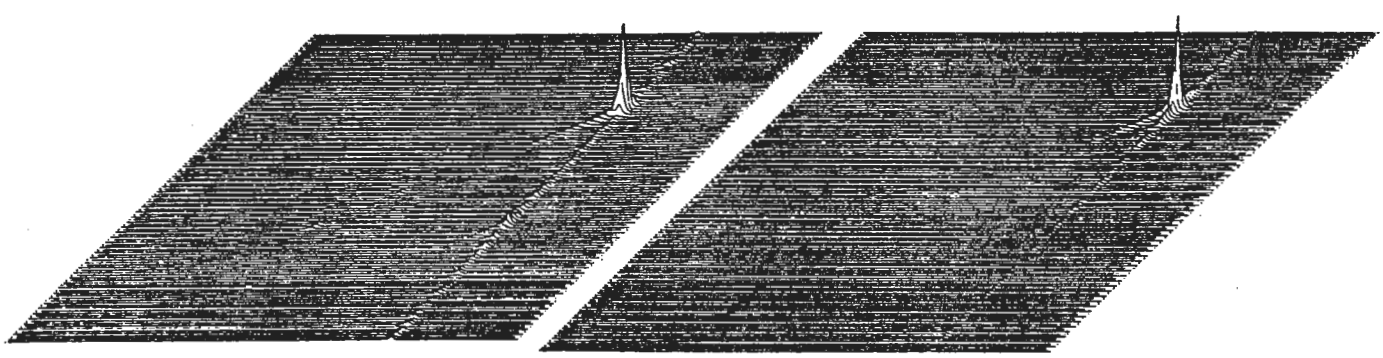

Fig. 3. 4-scan 2D COSY spectra of 1% acetone in 80% H_2O, locked on 19% acetone-d_6. Left, using hard 90° pulses which 'hit' the water magnetization; right, using actone-selective 11-pulses. Note the difference in the t_1 noise ridge. Spectral width in both dimensions is 50 Hz.

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

Professor Barry Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

(received 4/14/89)

Subject: Observation of Polyhydroxybutyrate in Soybean Bacteroids.

Dear Barry,

In connection with our ongoing program in the study of symbiotic plant systems, we have attempted to quantify the level of Polyhydroxybutyrate (PHB), an energy-rich storage polymer, in intact soybean root nodules using ^{13}C NMR spectroscopy. It is well known that the infecting bacteroids encapsulated within the root nodules contain up to 50% by weight, of PHB. Our initial attempts to observe this presumably mobile polymer (1) in intact nodules using our 400 MHz ^{13}C solution spectrometer gave marginal results. As reported earlier (2) only two resonances at 41.1 and 21.26 representing the CH_2 and CH_3 groups were evident. In addition, the CH_2 resonance, had less than 50% of the intensity of the CH_3 resonance (2), due to its lack of polymer backbone mobility (Fig. 1a).

Attempts to observe this polymer in the intact nodules with our Bruker 300 MHz MSL spectrometer in the ^{13}C CPMAS mode at various contact times gave even less satisfactory results. Presumably, the ^{13}C solid state spectra are dominated by carbohydrates, proteins, and lignin component resonances residing in the cortex surrounding the interior bacteroid-infected matrix. Even at contact times as long as 2 ms, little evidence of the PHB resonances appeared (Fig. 1b).

In order to circumvent this problem, we surgically removed the bacteroid-rich inner matrix of our two month old nodules, dried them, and examined them by ^{13}C CPMAS as a function of contact time. At a contact time of 0.1 msec, we observed a spectrum comparable th that given by the intact nodule at 2 msec, i.e., little evidence of PHB. However, as we increased the contact time, the more mobile PHB resonances began to dominate the spectrum (Fig. 1c). This is in agreement with Sander's findings (1) that PHB can be highly mobile. Evidently, it is essential to remove other relatively mobile polymers which dominate the spectra of these matrices before spectral quantitation of PHB can be accomplished (3). We suspect that ^{13}C solution spectra of the isolated bacteroid matrix will give comparable results.

Sincerely,

Philip Pfeffer | Dominique Rolin | Robert Dudley | Julian Schmidt

References

1) Sanders, K.M.; and Barnard, G. N. *FEBS. Lett.*, 231, 16, (1988)
2) Nicolay, K.; Hellingwerf, K. J.; Kaptein, R.; and Konings, W. N. *Biochim. Biophys. Acta*, 720, 250, (1982)
3) Jacob, G. S.; Garbow, J. R.; and Schaefer, J. *J. Biol. Chem.*, 261, 16785, (1986)

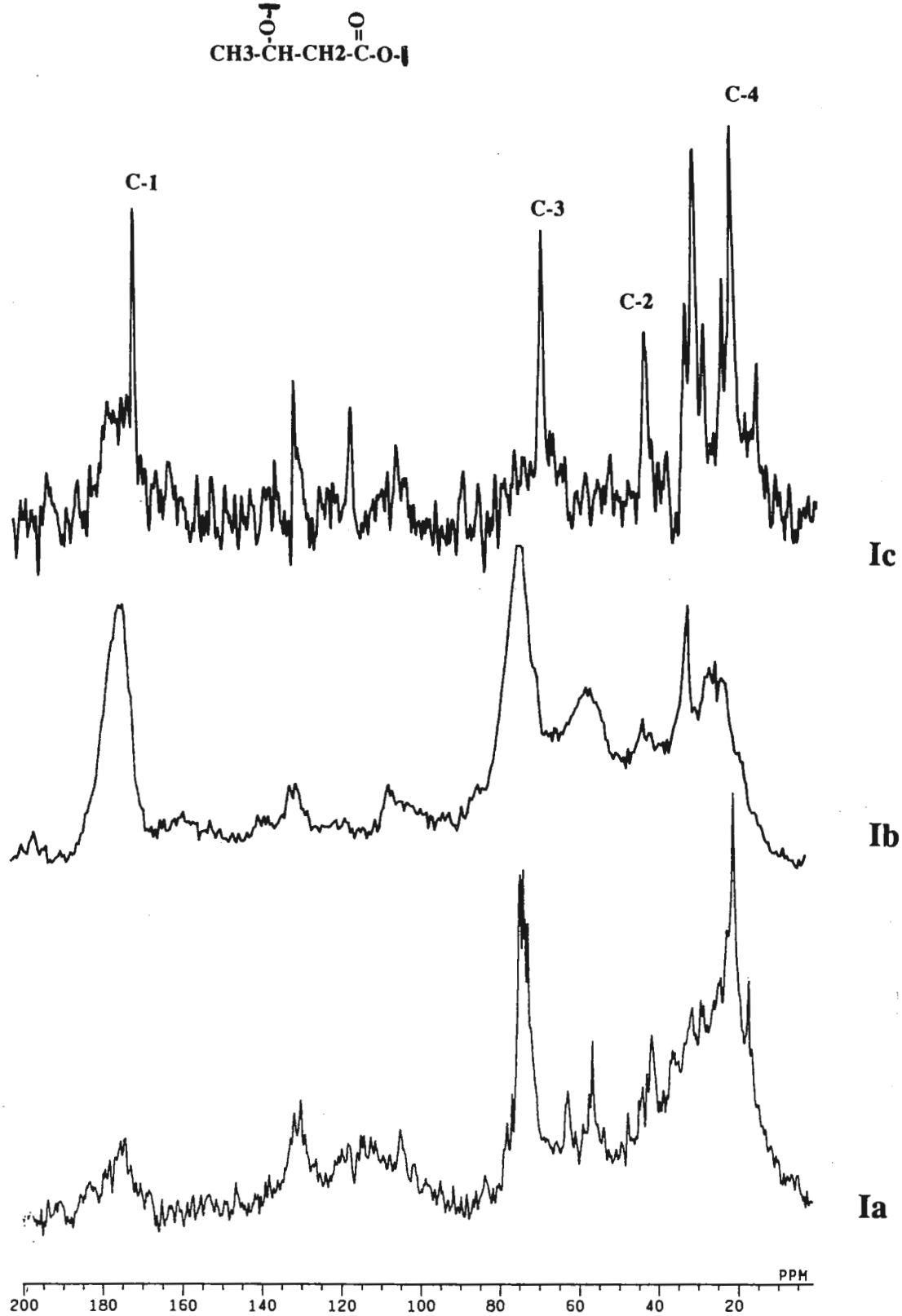

Fig.1 a) 100.4 MHz ^{13}C spectrum (1900 scans) of intact soybean nodules, perfused with an oxygenated solution of 50 mM glucose, 0.1 mM $CaSo_4$ and 15mM phosphate, pH 7.5; b) 75.47 MHz CPMAS ^{13}C spectrum of intact soybean nodules,contact time 2ms, 2400 scans; c) 75.47 MHz CPMAS ^{13}C spectrum of isolated bacteroids, contact time 15ms, 2400 scans (peak at 29.4 ppm is due to succinate).

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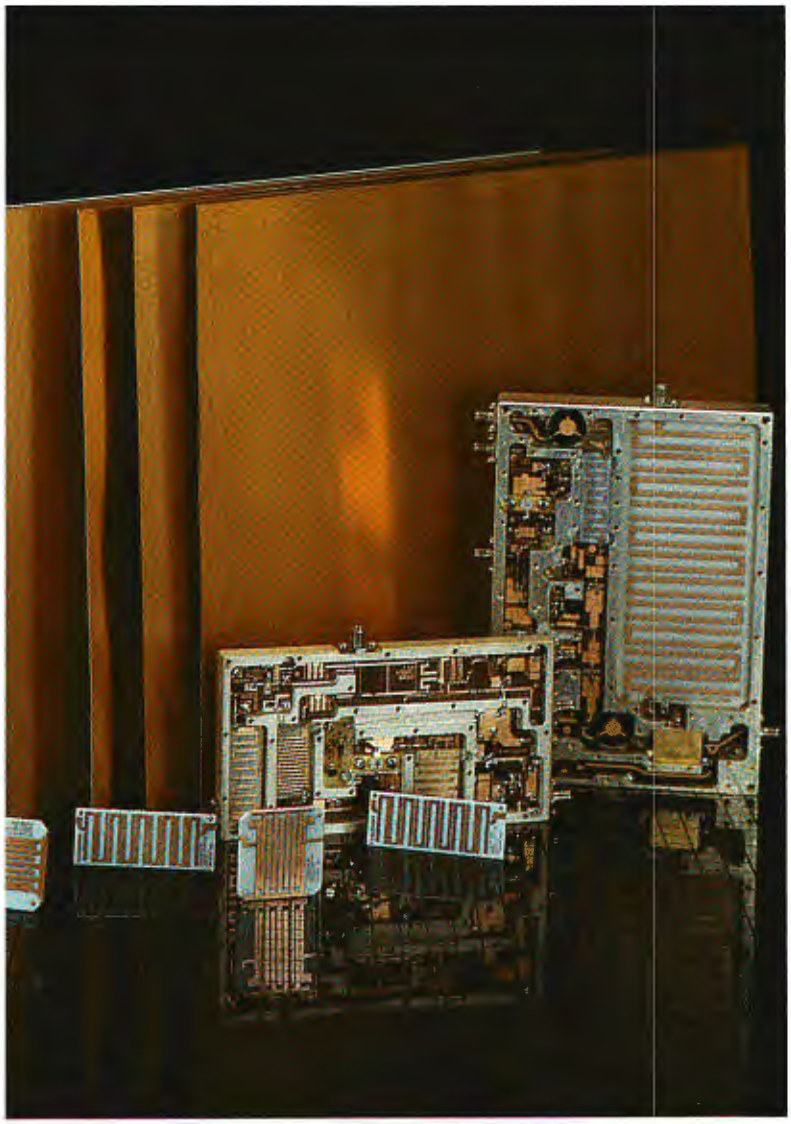

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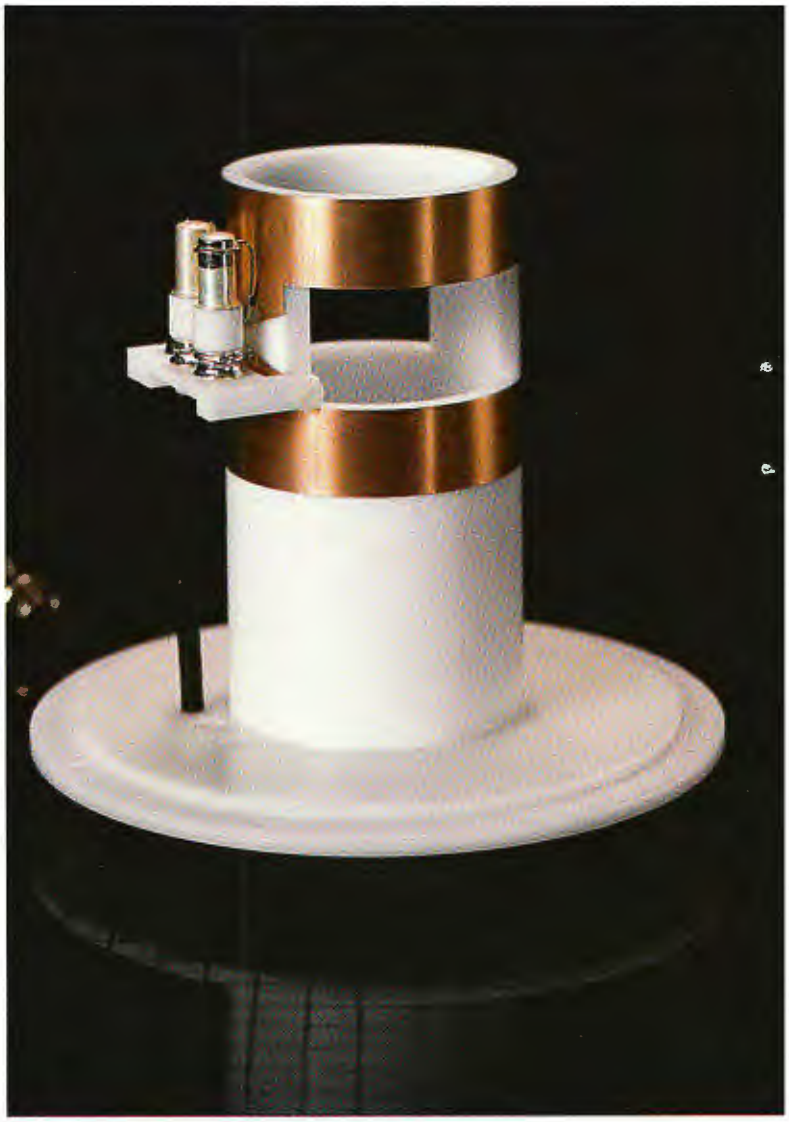

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SIEMENS

April 13, 1989
(received 4/17/89)

Optimizing Spectroscopic ^{19}F S/N on Whole Body Imagers

Dear Barry,

Normally ^{19}F in vivo spectroscopy on a whole body 1.5 T system involves exogenous compounds. In our studies of the chemotherapeutic agent 5-FU (5-fluoruracil), we have been struggling with S/N limits. During the time course of administration, at best, the concentration is no more than a few millimolar. Ways to increase available S/N are:

1) adding more spins (more compound, larger antenna, or enrichment)
2) increase number of acquisitions
3) increase field strength
4) increase the signal height intensity (shim better)

Numbers 1 and 2 are not feasible in the case of in vivo human ^{19}F spectroscopy. Number 4 is the easiest way to improve S/N in this case. The phantom results shown in Figure 1 compare a global shim versus a local shim using a modified DRESS[1] sequence. The acquisition was with a non-selective FID sequence and a 15 cm ^{19}F surface coil for the lower two spectra. As a way of 'adding more spins' the top spectra was acquired with an Adiabatic Half Passage[2] pulse. This gives more uniform (exclusively $\pi/2$) RF pulse throughout the B1 field of the surface coil. The phantom configuration was chosen to represent the liver or a tumor below the surface.

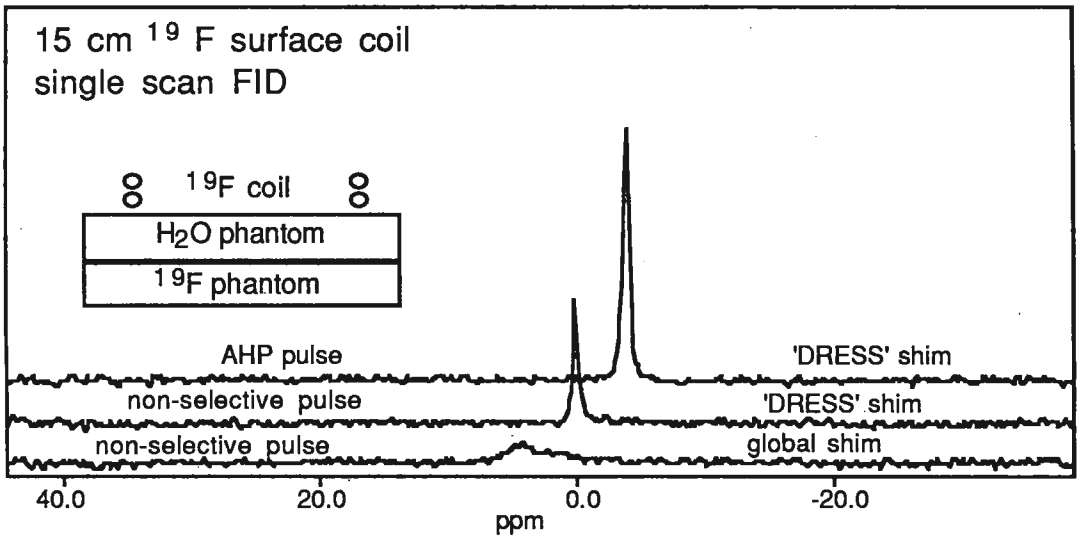
It should be noted that localized shimming is very tricky particularly if a different sequence is used to acquire. Since gradient pulse are used to localize the off-resonance effects can shift the localized position, and long time steady state effects can contribute to the field observed. Also, it should be noted, that almost any technique works with a phantom! We have not had real luck with patients, but we have been reticent to waste a data point on a patient by spending all the time developing a shim technique and never collect real data. For this experiment it is not feasible to use volunteers to improve technique!

Figure 2 shows the S/N level we see in a typical patient tumor. The linewidth indicates that shimming should improve the observed S/N. However, failing this, there is the age old fifth method for increasing perceived S/N - plotting differently! This is illustrated in Figure 3.

Sincerely,

Michael J. Albright
Dennis Atkinson
Richard Ong
Walter Wolf (USC)

1) Bottomley, P.A., Foster, T.B., Darrow, D.A., *J. Magn. Reson.*, **59**, 338 (1984).
2) Bendall, M.R., Pegg, D., *J. Magn. Reson.*, **67**, 376 (1986).



MAGNETOM 1.5 T

FIGURE 1

^{19}F/59.8MHz

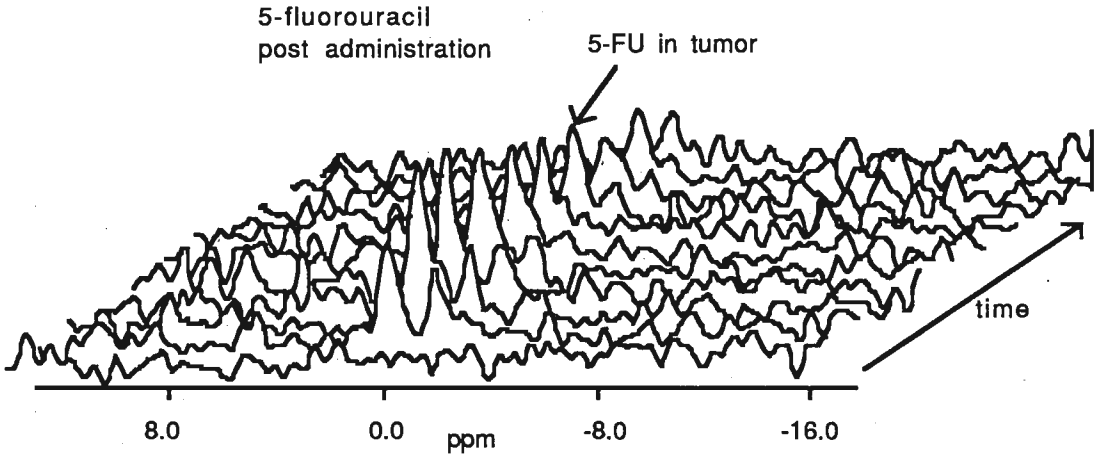


FIGURE 2

MAGNETOM 1.5 T

^{19}F/59.8MHz

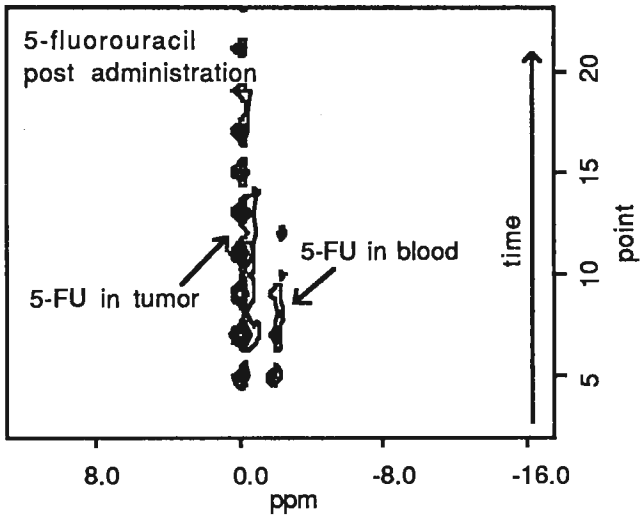


FIGURE 3

L.E.D.S.S.

UNIVERSITE JOSEPH FOURIER
GRENOBLE 1
SCIENCES. TECHNOLOGIE. MEDECINE

Laboratoire d'Etudes Dynamiques et Structurales de la Sélectivité
URA CNRS n° D 0332

ST-MARTIN-D'HÈRES, LE March 10, 1989
(received 3/30/89)

Dr. Bernard L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303
U.S.A.

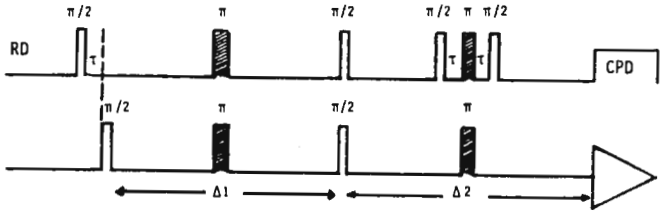
CINCH-EZ : It's a cinch !

Dear Dr. Shapiro:

When dealing with long-range ^{1,3}C-H correlations, we prefer utilizing 2D-COLOC type experiments (1) instead of a Freeman and Morris type experiment (2). In the former sequences the constant evolution time partly suppresses ^{1}J(CH) modulations on F2 dimensions and does not give loss of signal on F1 as t1 increases.

Unfortunately, as Perpick-Dumont et al. pointed out (3), both evolution (Δ1) and refocusing delays (Δ2) cannot be properly set by a classical 1D-INEPT experiment for protonated carbons. They proposed a derived INEPT sequence (CINCH-C) which suppresses polarization tranfer via ^{1}J(CH) coupling by combination of a TANGO and BIRD pulses.

We found that a variant of this sequence consisting of replacing the first TANGO pulse by a Low-Pass J-Filter gives better results in suppressing ^{1}J modulations. We dubbed it CINCH-EZ:



The smaller number of pulses (10 instead of 12) and the greater efficiency of the Low-Pass J Filter (?) may account for these better results.

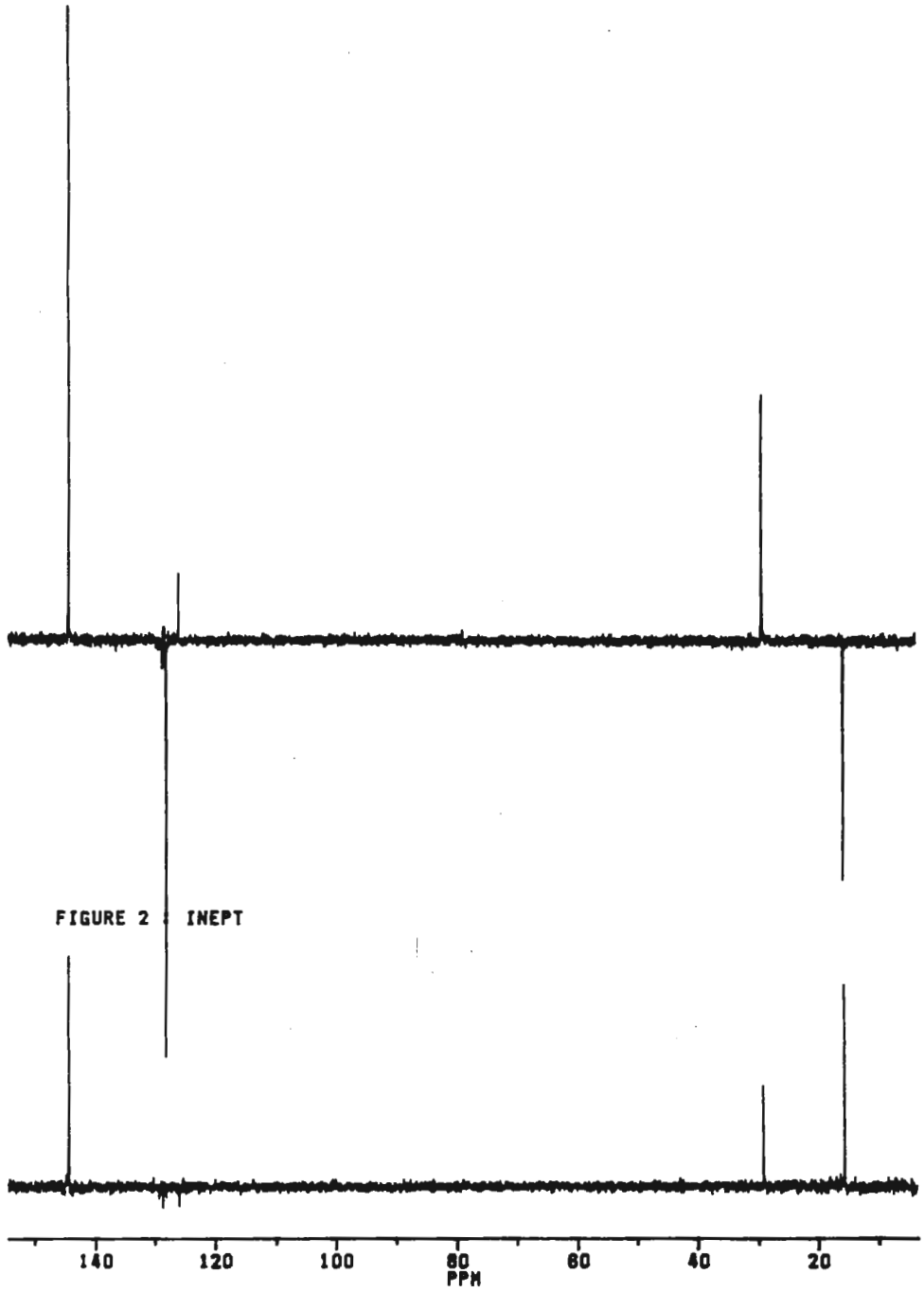
Figures 1 and 2 show the spectra we have obtained from the CINCH-EZ and classical INEPT experiments on ethyl benzene with identical parameters (Δ1 set for $^{n}J = 4,5\ H_2$).

Sincerely yours,

Duc Astin — Julian Garcia — Claude Morat

(1) J. Magn. Reson., 57, 331 (1984)
(2) J. Am. Chem. Soc., 100, 320 (1978)
(3) J. Magn. Reson., 75, 414 (1987)
(4) Magn. Reson. Chem., 26, 24 (1988)

FIGURE 1 : CINCH-EZ



RD = 3 s ; τ = 3.5 ms ; Δ1 = 120 ms ; Δ2 = 30 ms ; NS = 16

STAFF NMR RESEARCH ASSOCIATE POSITION, UNIVERSITY OF CA, IRVINE.
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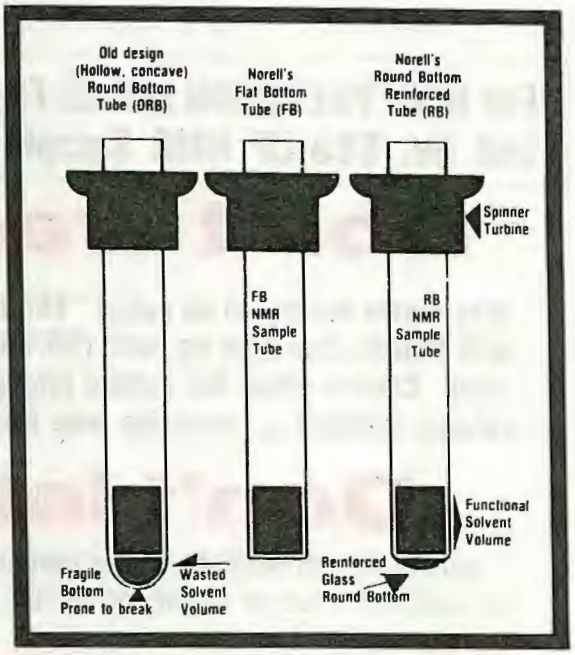

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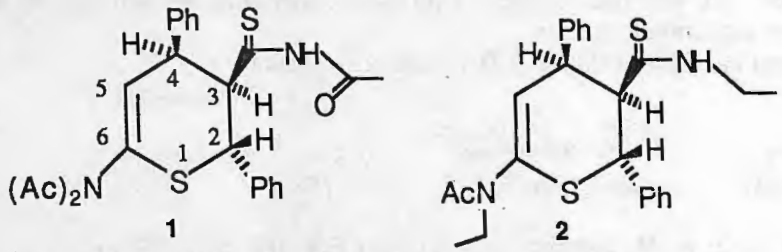
Professor Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303
U.S.A.

13 March 1989
(received 3/29/89)

Subject: **Strange negative peaks in the $^1H\{^1H\}$ 1D NOE difference spectra of some thiopyran derivatives**

Dear Professor Shapiro,

Recently we have investigated the structures of the following thiopyran compounds

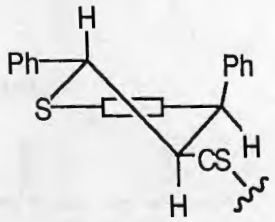


Characteristic ^1H chemical shifts and H,H couplings are as follows:

1 δ ($CDCl_3$): 4.18 (1H, dd, H-4); 4.85 (1H, d, H-2); 5.31(1H, broad at 297K, sharp dd at 323K, H-3); 6.08 (1H, d, H-5). J(H-2,H-3)=11.3Hz; J(H-3,H-4)=4.5Hz; J(H-4,H-5)=6.5Hz.

2 δ ($CDCl_3$): 4.23 (1H, dd, H-3); 4.38 (1H, dd, H-4); 4.57 (1H, d, H-2); 5.93 (1H, d, H-5). J(H-2,H-3)=11.9Hz; J(H-3,H-4)=4.8Hz; J(H-4,H-5)=6.2Hz.

The relative configurations and the predominant conformation of the thiopyran ring were readily and unambiguously established from the relevant vicinal couplings as well as from proton-proton NOE difference measurements, leading to the following stereostructure for both compounds:



One striking difference between the two compounds is, firstly, that in **1** H-3 gives a rather broad signal at room temperature at 400 MHz (couplings are almost completely washed out); and secondly: H-3 is more than 1 ppm downfield of its value in **2**. By increasing the temperature to ca. 50 °C the H-3 signal in **1** sharpens, and shows a slight upfield shift. All this can be conveniently accounted for by assuming the presence of a weak internal hydrogen-bonding between H-3 and the NHAc carbonyl oxygen.

The really intriguing phenomenon, however, is that in the room-temperature NOE difference spectra of **1**(pre-irradiation times 4s), irradiation of H-2 gives a negative peak on H-3, and vice versa. (The effect is ca. -3% when measured in $CDCl_3$, but much larger in DMSO - see Figure). All other NOEs are perfectly "normal" (positive), as it is expected in a molecule of this size. The negative peaks disappear at increased temperatures (giving zero NOEs in accordance with the trans-diaxial relationship between H-2 and H-3),

apparently in relation to the simultaneous sharpening of the H-3 signal. Also, these negative peaks are absent in the NOE spectra of **2**. At present, we are still trying to find an adequate explanation to the phenomenon. There are, however, a number of points that are worth noting:

a, Considering the relatively large separation of H-2 and H-3 in **1**, the negative peaks certainly cannot stem from irradiation spill-over (using an irradiation power of 53L on our Bruker AM400 instrument).

b, Non-selective T_1 relaxation times are ca. 1 s for *all* ring protons. (We checked this just to be absolutely sure that there is "nothing wrong" with the extreme narrowing condition).

c, Considering the stereochemistry involved, as well as the size of the negative peaks (especially in DMSO) the possibility of a three-spin effect[1] can be discarded.

d, Since the spectrum is clearly first-order at 400 MHz, negative peaks due to strong couplings[2] are also out of the question.

e, The possibility of saturation transfer via a slow chemical exchange between H-2 and H-3 cannot be entirely ruled out, since both protons are activated. However, such an exchange should also bear the feature of retaining the above depicted relative configurations of the carbons involved. Devising a mechanism that should fulfil this aspect of the phenomenon is quite difficult indeed. (We do have some farfetched ideas, though). Unfortunately no other, more direct proof for a possible exchange is available: neither H-2, nor H-3 are exchangeable with deuterium; coalescence could also not be observed. [We went up to 140 °C (about the highest temperature the compound can tolerate for a few minutes) in DMSO at 400 as well as at 90 MHz]. Also, the fact that the effect disappears at increased temperatures seems to be somewhat contradictory to what one would expect from a "well-behaved" saturation transfer.

For the time being, we are trying to find some suitable analogues to get a better feel for our mysterious negative peaks. We are also testing the possibility that what we are looking at is an intermolecular exchange rather than intramolecular.

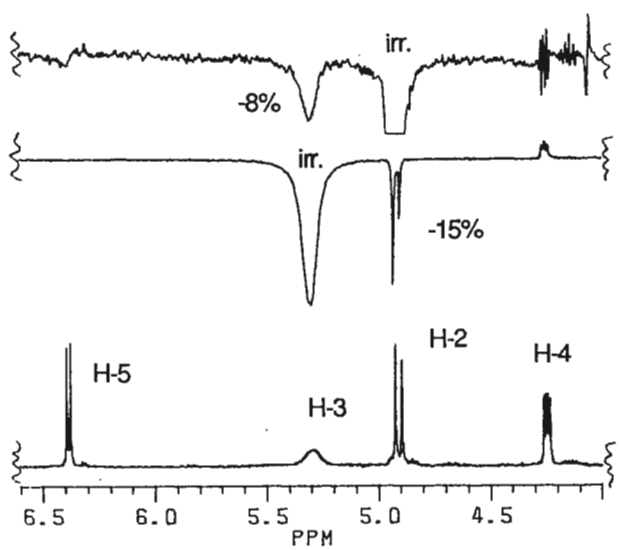
Please credit this contribution to J. D. Kennedy's account.

Yours sincerely,

Cs. Szantay, Jr. C.W.G. Fishwick D.R. Hill

1. D. L. Hall and J. K. M. Sanders, *J. Am. Chem. Soc.*,**102**, 5703 (1980).
2. J. Keeler, D. Neuhaus and M. P. Williamson, *J. Magn. Reson.*, **73**, 45 (1987).

One of us (Cs. Sz.) would like to thank Dr. G. A. Morris for a helpful discussion.



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The Department of Chemistry, University of Wisconsin-Madison is seeking a Director for the NMR Laboratory in the Chemistry Instrument Center. The responsibilities include training graduate students in the theory and application of NMR spectroscopy, collaborative research with faculty and graduate students, and operation and administration of the NMR facility. Experience with solid state and high-resolution liquid samples is desirable. The facility presently operates five high-field (4.7 Tesla to 11.5 Tesla), high resolution, multinuclear FT-NMR spectrometers; a second 11.5 Tesla multinuclear instrument and a wide-bore 7.0 Tesla solids instrument will be added in the summer of 1989. Interested parties should send resumes and arrange for three letters of reference to be sent to: Professor T. C. Farrar, Department of Chemistry, University of Wisconsin, Madison, WI. 53706. The University of Wisconsin-Madison is an Equal Opportunity/Affirmative Action Employer and encourages women and minorities to apply.

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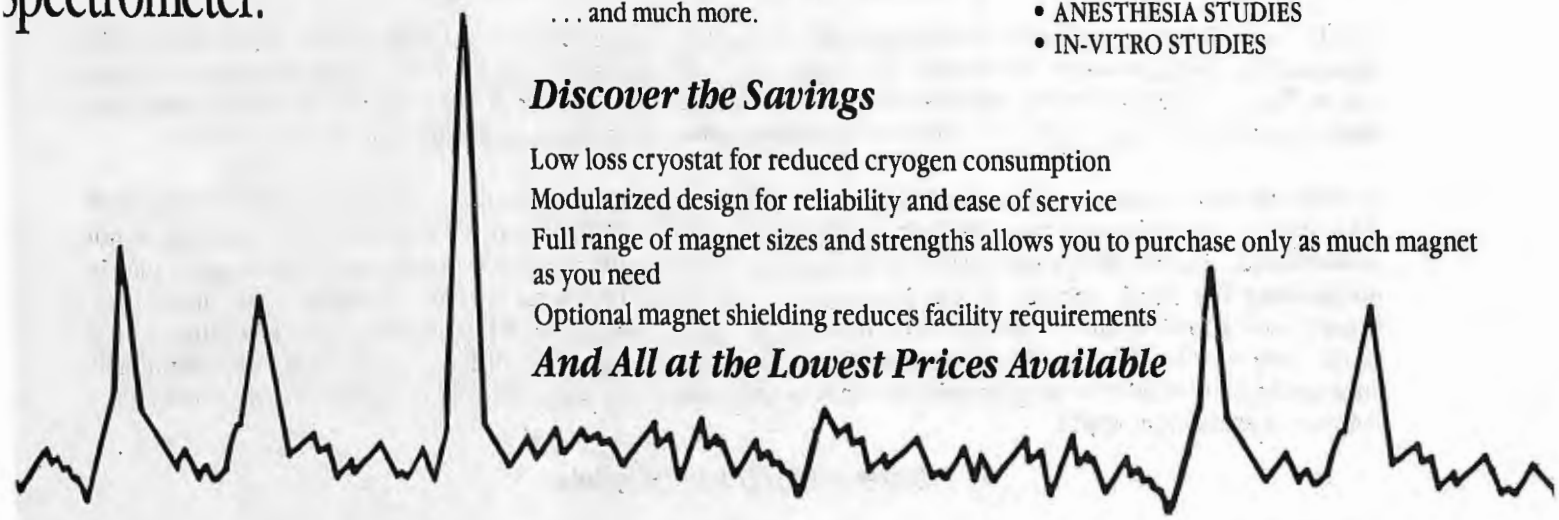

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TEXAS A&M UNIVERSITY
NMR
NEWSLETTER

No. 368
May 1989

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Subscription Renewals for the October 1989 - September 1990 Newsletter Year.

Subscription renewal invoices for the October 1989 - September 1990 Newsletter year will be mailed out on or about June 30, 1989. If you should receive an invoice and do not get one by, say, July 15, please contact me without delay. Your kind *prompt* attention to these invoices will be greatly appreciated. In order to keep costs and my work load down to a tolerable level, please initiate payment for receipt by September 5, 1989.

Kindly note that (i) prepayment is required, (ii) all payments must be in US dollars, net of all bank or other charges, (iii) checks must be drawn on a U.S. bank or a U.S. branch of a foreign bank, (iv) checks must be made out to 'Texas A&M University', but mailed to B. L. Shapiro, TAMU NMR Newsletter, 966 Elsinore Court, Palo Alto, CA 94303, U.S.A., (v) the use of commercial subscription agencies to make payment is not acceptable

In anticipation of revenues from Advertising and Sponsorships continuing to develop, I have decided to keep both subscription and advertising rates at their current levels for the 1989-90 year. I hope that my optimism is not unwarranted. Let me once again draw your attention to the vital role which our **Advertisers** and **Sponsors** play in maintaining the fiscal viability of the Newsletter. It would be useful for our Subscribers to make their appreciation known to the Advertisers and Sponsors for this service to the NMR public. With subscription fees as the only source of funds, the Newsletter would cease to exist in short order. Additional Advertising and Sponsorships are needed to keep up with the natural increases in the costs involved in publishing the Newsletter - can your organization help??

Newsletter Publication Schedule.

I will be away from my office for the period June 20 through July 16, 1989. My incoming mail and telephone answering machine will be monitored during this period, however, so keep those technical contributions, advertising insertion orders and payments coming, please. The actual Newsletter publication schedule will remain essentially unchanged, at least to first-order. My plans for the above period include attendance at the July 10-14 Royal Society meeting at the University of Warwick, where I hope to see many old (perhaps *longstanding* would be more felicitous) friends and mayhap some new ones. These Royal Society meetings are always worthwhile and most pleasant, and attending these well-organized gatherings is highly recommended for both participants and 'accompanying persons'.

B.L.S.
1 May 1989

CSI 2T Applications

Shielded Gradients and Localized Spectroscopy

Eddy current effects are the leading cause of errors and lack of consistent results in gradient localization methods. It is not surprising, then, that actively shielded gradients, which have dramatically reduced eddy currents, represent a significant technology advance for all forms of B_o gradient volume localization and spectroscopic imaging methods. The fast rise time and high gradient strength characteristics of the coil used in these experiments are also important.

Even without pre-emphasis, shielded gradients recover fast enough to obtain spectroscopic information at 1 msec or less after a strong gradient has been turned off (Fig. 1).

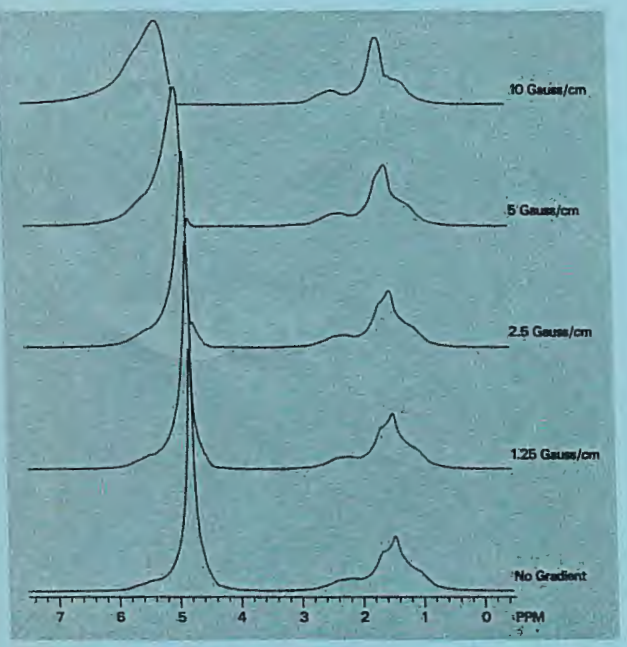

Fig. 1—Using an oil/water phantom, a 10 G/cm gradient will create a water frequency profile extending from 156 KHz to 280 KHz away from normal water resonance. Residual gradient effects of less than 0.01% (50 Hz at 10 G/cm) are observed in a spectrum acquired beginning 1 msec after a 20 msec gradient pulse.

As an example, a 4DFT spectroscopic imaging technique can resolve the four frequency domains that are associated with an NMR signal from an object: x-, y-, z-spatial coordinates and chemical shift δ. The above technique can be a practical alternative to single volume localized spectroscopy. This method allows phosphorous spectra to be obtained from well-defined regions as demonstrated in the following experiment, which was carried out on a GE CSI 2T system using high-strength, shielded gradient coils (Fig. 2). The phase-encode time is kept short (on the order of the dwell-time) to minimize phase-errors in the final spectra, as well as to avoid loss of signal due to T2 decay, which is significantly short in biological phosphates.

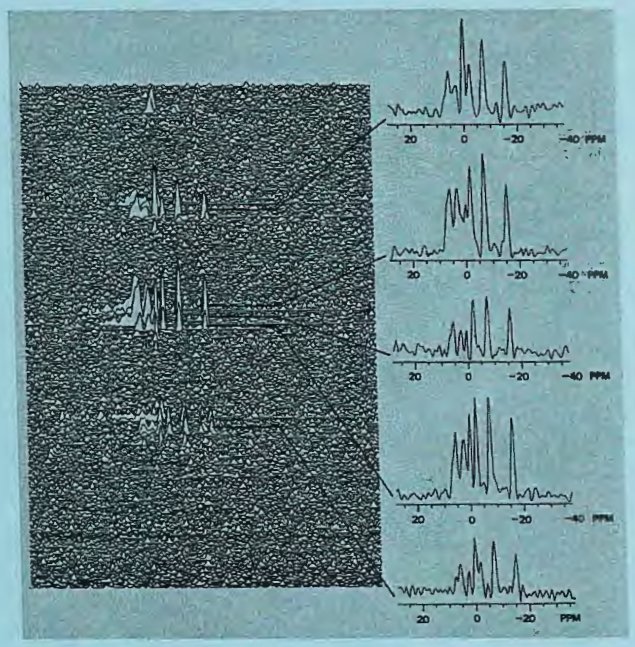

Fig. 2—Stacked plot showing 512 phosphorous spectra from 60 mm cubed region of a live rat. Each trace corresponds to 7.5 mm cubed region (voxel) from within the region of interest. The offset traces clearly show the achievable spectra and spatial resolution of the technique, as well as demonstrating localization of the liver phosphorous metabolites from that of overlying skeletal muscle. Total acquisition and processing time was two hours.

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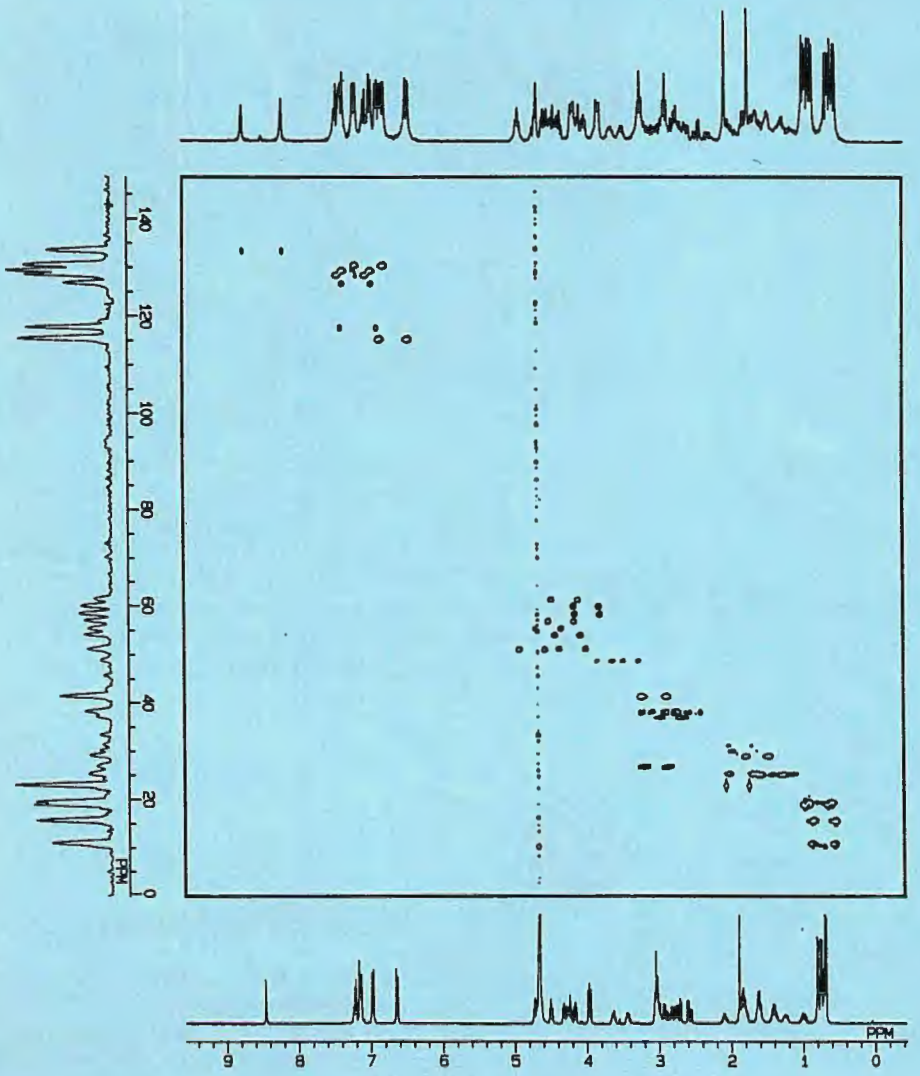

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