TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 375

December 1989

Continued on page 76

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-d_4	CD_3COOD	99.5%	1.12	17	118	0.551 (32)
D-120	Acetic Acid-d_4 (TFA)		99.5%				
D-13	Acetone-d_6	CD_3COCD_3	99.8%	0.87	-94	57	0.460 (20)
D-121	Aceonte-d_6 + 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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WCV-XL (XL-100)	11" X 26"	XL-100 (CF and FT)	Gridded-Two Color
WCV-XLFT-100	11" X 26"	XL-100 (CF and FT)	Gridded-Two Color
WCV-XL-200	11" X 26"	XL-200, XL-300, XL-400	Gridded-Two Color
WCV-20 (CFT-20)	11" X 16 3/4" X 17"	CFT-20, FT-80, FT-80A All Models 16 1/2" or 16	Gridded-Two Color Blank

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FORTHCOMING NMR MEETINGS

Workshop "NMR and Structure of Biomolecules", March 4-9, 1990; Gainesville, Florida; Contact: W. S. Brey, University of Florida, - see Newsletter 375, 68.

Workshop on In Vivo Magnetic Resonance Spectroscopy III, March 29 - April 1, 1990, San Francisco, California; San Francisco, California; Contact: Dr. M. W. Weiner or Dr. G. B. Matson, Magnetic Resonance Unit, Veterans Administration Medical Center, 4150 Clement Street (11D), San Francisco, CA 94121; (415) 750-2146.

31st ENC (Experimental NMR Conference), April 1-5, 1990; Asilomar Conference Center, Pacific Grove, California; Contact: ENC, 750 Audubon, East Lansing, MI 48823; (517) 332-3667; Attendance: 1,200.

Frontiers of Polymer Characterization by NMR Spectroscopy, Symposium at the American Chemical Society National Meeting, April 22-27, 1990, Boston, Mass.; See Newsletter 372, 54.

Workshop of Special Topics in Medical Magnetic Resonance, sponsored by the Society of Magnetic Resonance in Medicine and the National Research Council of Canada, July 23-27, 1990; Whistler Mountain, BC, Canada. Contact: L. Forget - see Newsletter 374, 46.

Expanding Frontiers in Polypeptide and Protein Structural Research, sponsored by the National Research Council of Canada, July 23-27, 1990; Whistler Mountain, BC, Canada. Contact: L. Forget - see Newsletter 374, 46.

Tenth International Biophysics Conference, sponsored by the International Union of Pure and Applied Biophysics and the National Research Council of Canada, July 29 - August 3, 1990; Vancouver, BC, Canada. Contact: L. Forget - see Newsletter 374, 46.

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. 377 (February) ------ 19 January 1990
No. 378 (March)------- 16 February 1990
No. 379 (April) ----------16 March 1990
No. 380 (May)---------- 20 April 1990

EMORY UNIVERSITY
Department of Chemistry

1515 Pierce Drive
Atlanta, Georgia 30322
404/727-6585

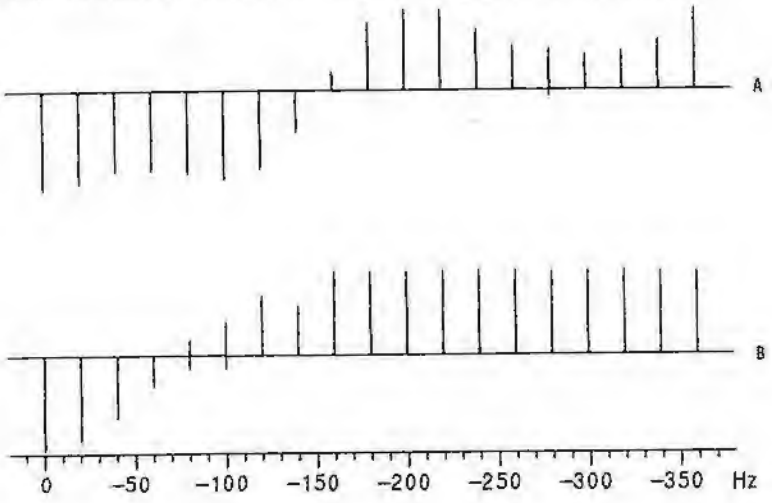
November 2, 1989
(received 11/7/89)

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

Dear Barry:

Selective Excitation With Composite 180° Pulses

There has been a great deal of interest in using selective excitation in a variety of NMR applications. Although shaped pulses are probably the best way to produce a well defined rectangular spectrum of excitation, the ability to generate these is still not a common feature of most NMR spectrometers. Many researchers have turned to low power square wave pulses as an approximation to the ideal. In recent years a number of composite pulses such as the $90^{\circ}_{x}-180^{\circ}_{y}-90^{\circ}_{x}$ composite 180°, and the WALTZ and MLEV have been put forward to compensate for RF inhomgeneity and to improve decoupling efficiency respectively. These sequences have the property that the frequency distribution of their excitation is much more rectangular than that of a single square wave pulse. The offset frequency dependence of such pulses is discussed at length in a review by Levitt (Prog. in NMR Spectroscopy, V. 18, p.61 (1986)). Such composite pulses have generally been used to "selectively" excite a wide region more uniformly, such as the whole ^{1}H without depositing RF power outside that region. By the same token, reducing the power level used in such composite pulses, can result in cleaner excitation of narrower regions than is realized with a single "soft" square wave pulse. This can offer an improvement accessible on most spectrometers in the absence of shaped pulse capabilities. The offset dependence of the composite 180 (A) relative to a square wave 180° (B) pulse is shown in the figure below. The RF power was 120 Hz in both cases. Improved selectivity of the composite pulse excitation has proven to be valuable for selective inversion of the H3' protons in oligonucleotides without inverting the nearby H4', and H5' and H5" sites. We have applied this approach to advantage in carrying out selective proton detected H3' to ^{31}P COSY spectra of oligonucleotides for the purpose of measuring vicinal heteronuclear coupling constants (Sklenar and Bax, J. Amer. Chem. Soc., V. 109, 7525 (1987)).



Yours,

David Live

THE OHIO STATE UNIVERSITY

Department of Chemistry

120 West 18th Avenue
Columbus, OH 43210-1173
Phone 614-292-2251

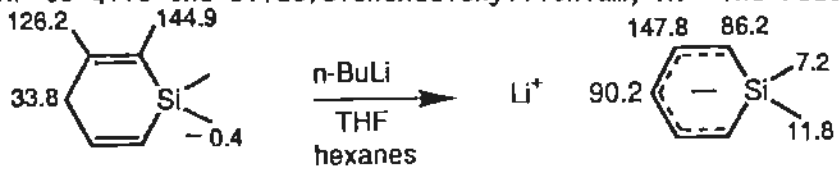
October 16, 1989
(received 10/28/89)

Dr. B. L. Shapiro
TAMU Newsletter
960 Elsinore Court
Palo Alto, California 94303

Silacyclohexadienyllithium

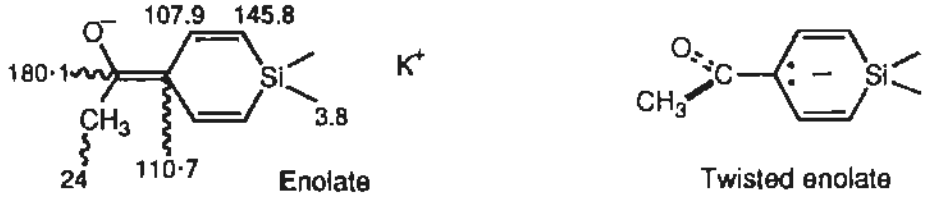
Dear Barry:

NMR difference spectroscopy tends to be used mostly by biochemists and anyone who deals with small changes in complicated molecules. Not so well known is analysis of crude reaction mixtures. Siladiene, **D**, impure, is easily deprotonated with butyllithium in THF to give the silacyclohexadienyllithium, **A**. The reaction mixture also



Diene Anion

contains hexanes from the butyllithium solution. The ^{13}C spectra before, **D**, and after reaction, **A**, look similar but subtracting the two reveals the spectrum of the silacarbanion, **A**, right side up, and starting material, upside down, see Figure. The numbers around the structures are the ^{13}C shifts. Only in this way do we find the methylene resonance of siladiene. Also one of the carbons of **D** and **A** have almost the same shift. We wondered whether the shifts in **A** reveal anything about possible overlap of silicon with the π system resulting in cycloconjugation. I think not, so far. Needless to say we have since checked all this with cleaner samples. Along similar lines we have acylated **A** and prepared the potassium enolate salt **E** in diglyme in



Enolate Twisted enolate

order to measure the barrier to rotation about the carbonyl carbon-ring bond. Stabilization of the transition state for rotation, might imply cycloconjugation. At first glance it seems the rate of acetyl rotation is normal for an enolate.

Best regards from Ohio State.

Gideon

Sincerely,

Christopher J. Kolp

Gideon Fraenkel
Professor of Chemistry

Christopher Kolp
Graduate Research Associate

GF/cag

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Bore With RT Shims And Gradients (cm)	26.5	26	33	15	26.5	31	15
Helium Evaporation (ml/hr)	50	50	50	50	55	60	50
Nitrogen Evaporation (ml/hr)	400	400	400	400	450	500	400
Half Length (mm)	350	275	570	396	460	735	575
5 Gauss Line — Radial From Center (m)	3.4	3.2	4.7	3.7	5.3	6.4	5.1
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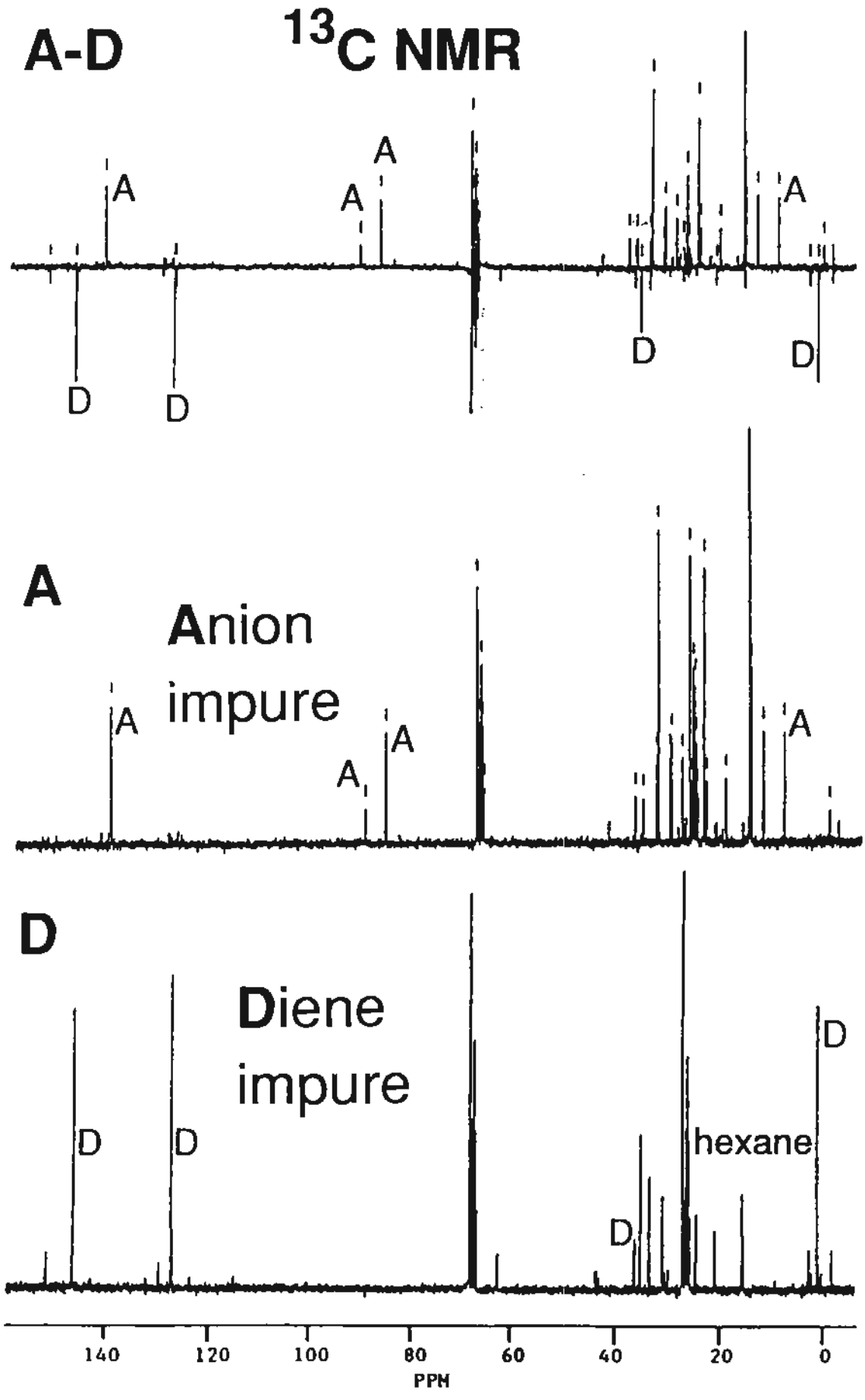
A-D
^{13}C NMR
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A
D
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impure
D
D
D
D
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CSI 2T Applications

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).

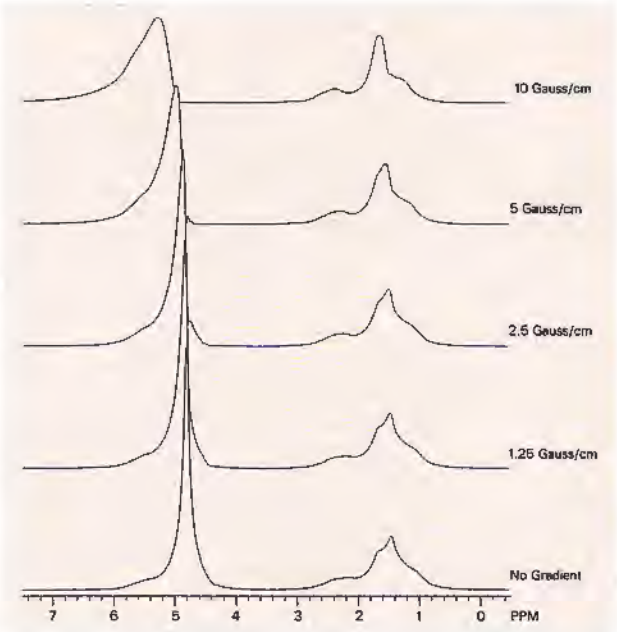

Fig. 1—Using an oil/water phantom, a 10 G/cm gradient will create a water frequency profile extending from 156 KHz to 280 KHz away from normal water resonance. Residual gradient effects of less than 0.01% (50 Hz at 10 G/cm) are observed in a spectrum acquired beginning 1 msec after a 20 msec gradient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

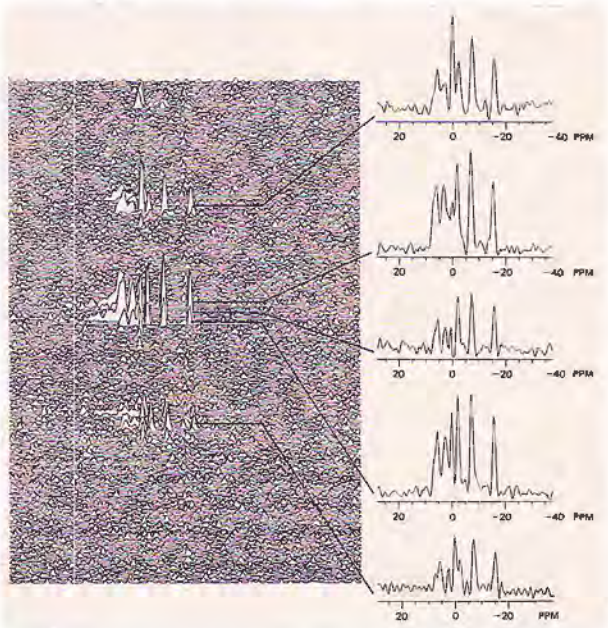

Fig. 2—Stacked plot showing 512 phosphorous spectra from 60 mm cubed region of a live rat. Each trace corresponds to 7.5 mm cubed region (voxel) from within the region of interest. The offset traces clearly show the achievable spectra and spatial resolution of the technique, as well as demonstrating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

GE NMR Instruments

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Professor B. L. SHAPIRO
966 Elsinore Court
Palo Alto
California 94303
Etats Unis

Theix, 1989 october 23
(received 10/30/89)

Dear Professor Shapiro

NMR and Collagen-Hydration

The effect of collagen hydration and cross-linking state was investigated by Differential Scanning Calorimetry and NMR studies. Intramuscular collagen from animals with different ages had different polymerisation states. All samples were hydrated under well defined Aw conditions prior to NMR and DSC analysis.

DSC determines the amount of unfreezable water, the enthalpy ΔH and temperatures of transition of collagen to gelatin .

The proton NMR relaxation times of water in interaction with protein provide information about the dynamics of water molecules and their local environment. The cross-relaxation between water and collagen has been specially studied as a function of temperature between -20° and 100°C.

From the temperature dependency of cross relaxation rates (R+), the dynamic of water molecules and the exchange times were determined. The different motions were temperature and water content dependent (figure 1 &.2)

NMR and DSC are complementary methods to characterize the hydration and cross-linking state of collagen.

Yours sincerely

Madeleine BONNET

Jean Pierre RENOU

figure 1

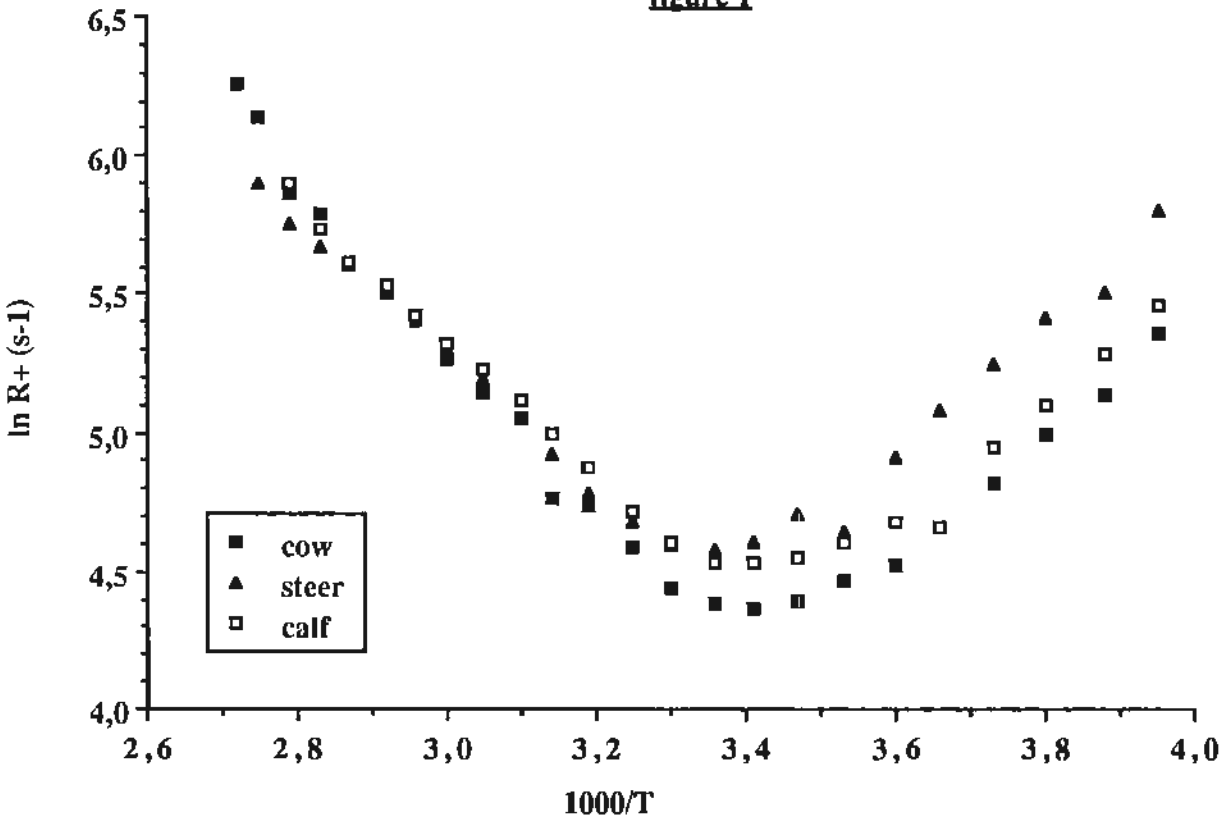
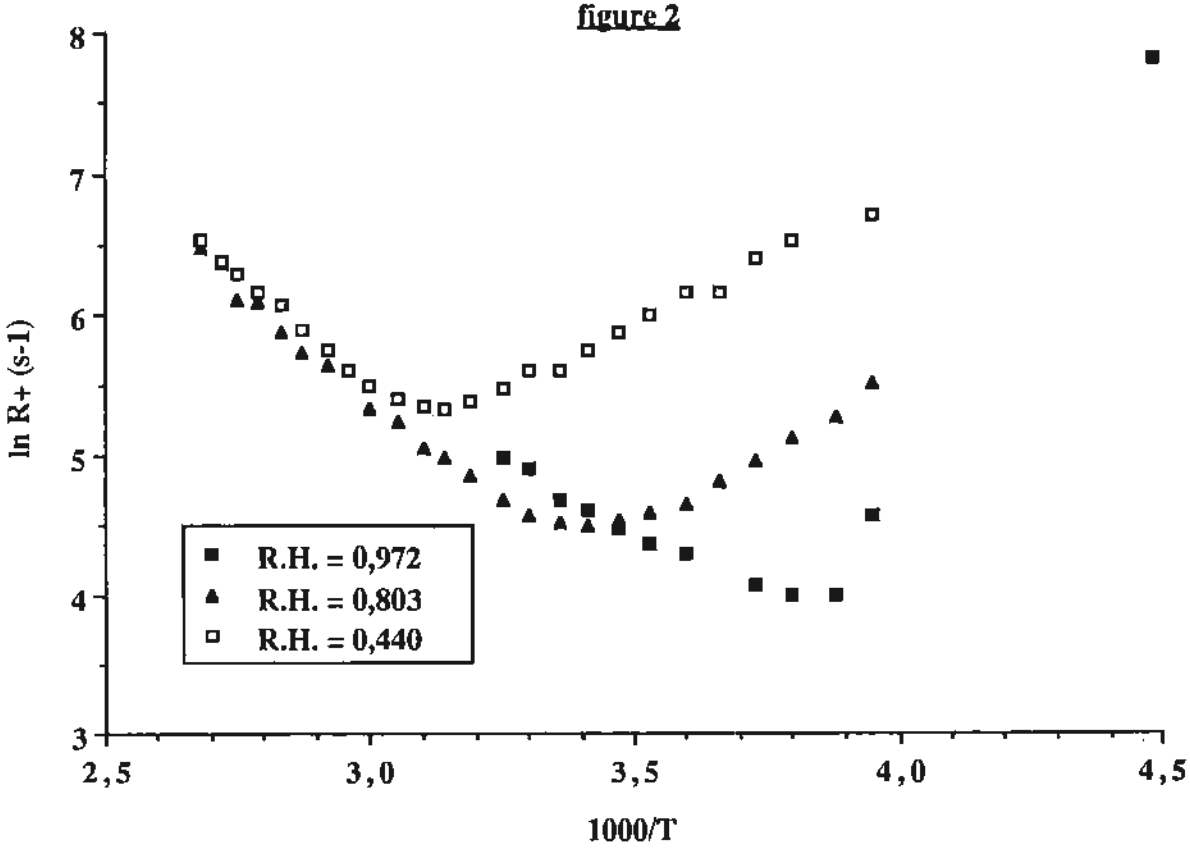


figure 2



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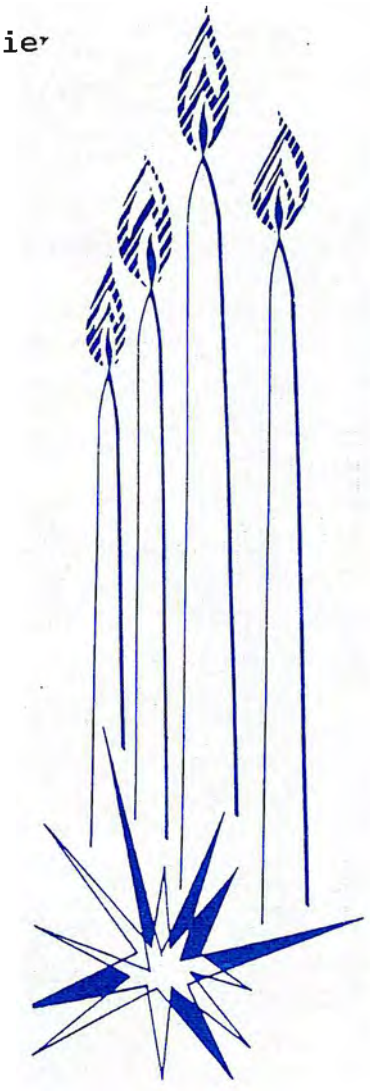

Doty Scientific, Inc.

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L.E.D.S.S.

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Laboratoire d'Etudes Dynamiques et Structurales de la Sélectivité
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ST-MARTIN-D'HÈRES, LE 2 novembre 1989
(received 11/6/89)

N/RÉF. Dr B.L. Shapiro
V/RÉF. TAMU NMR Newsletter
OBJET 966 Elsinora Court
Palo Alto, CA 94303

CALIBRATION OF BROADBAND HETERONUCLEAR DECOUPLING

Dear Dr Shapiro,

It is well known that the introduction of the composite pulse sequence dubbed WALTZ-16 (J. Magn. Reson, 52, 335, 1983) has brought noteworthy improvement in the heterodecoupling field. For measuring quantitatively the gain in decoupling width, we tested the effectiveness of WALTZ-16 versus conventional broadband decoupling (BB) on the three spectrometers located in our research building.

Figures a, b and c show examples of ^{13}C spectra of a benzene solution (doped with $Cr(acac)_3$ for faster repetition time) ^{1}H decoupled by BB (left) or WALTZ-16 sequence (right : MOD = 1 with Pulse Programmer or CPD with Process Controller) carried out on WP 80, AC 200 and AM 300 Bruker instruments.

From these results, it appears that i/ the efficiency of WALTZ-16 is by far superior to BB <u>but</u> ii/ depends on the spectrometer !($\gamma B_{90\ \%} \simeq 6$ times larger on WP 80 ; $\simeq 5$ times on AC 200 ; $\simeq 3.5$ times on AM 300).

In fact, we verified that on the AM 300, with the 5 mm $^{1}H/^{13}C$ dual probe, the WALTZ-16 sequence is satisfactory <u>even</u> at the low decoupling power mode (DP = OL corresponding to $\simeq$ 0.2 watt ; $\gamma B_{90\ \%} \simeq 13$ ppm; P9 = 143). This outstanding performance permits us to carry out selective heteronuclear experiments without switching between low and high power decoupling modes, thus preserving the lifetime of relays !

Sincerely,

Duc Astin — Julian Garcia — Jean-Pierre Gaude — Claude Morat

ADRESSE GEOGRAPHIQUE : BATIMENT CHIMIE RECHERCHE - 301, RUE DE LA CHIMIE - DOMAINE UNIVERSITAIRE - SAINT-MARTIN-D'HÈRES - GIERES
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L.E.D.S.S.

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SCIENCES. TECHNOLOGIE. MEDECINE

Figure a

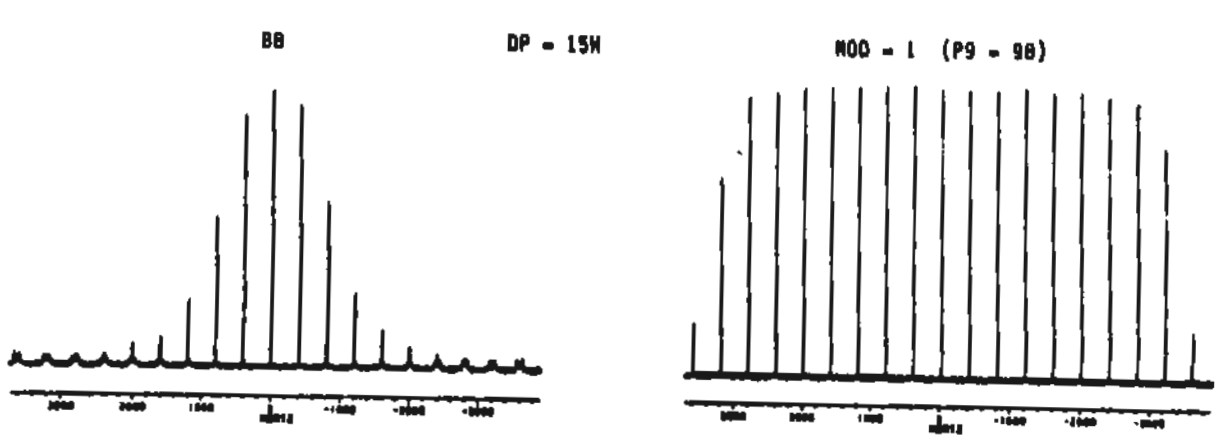


Figure b

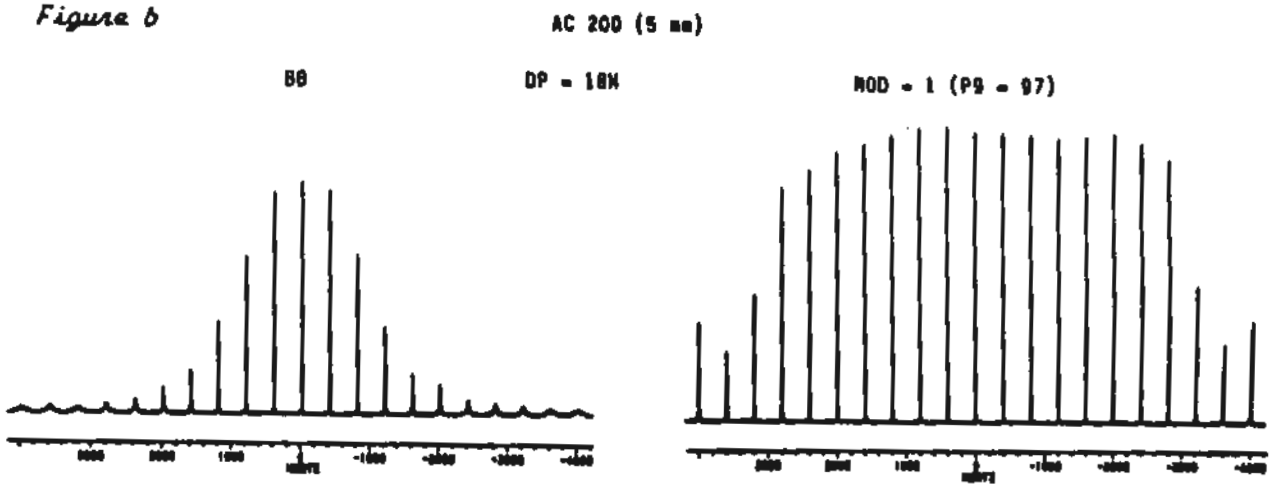
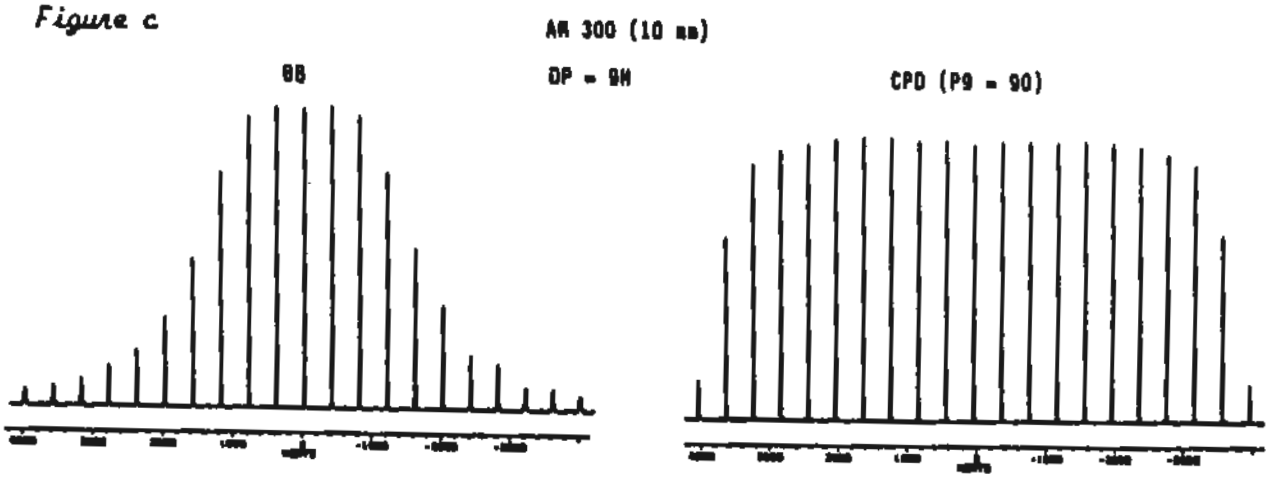


Figure c



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DEPARTMENT OF CHEMISTRY

GORLAEUS LABORATORIES

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

Your reference	Your letter	Our reference	Date	5, Einsteinweg
		CE/ML	10-23-'89 (received 11/2/89)	Phone (31) 71 - 272727 direct dialling (31) 71 - 27 4230 telefax (31) 71 - 274537

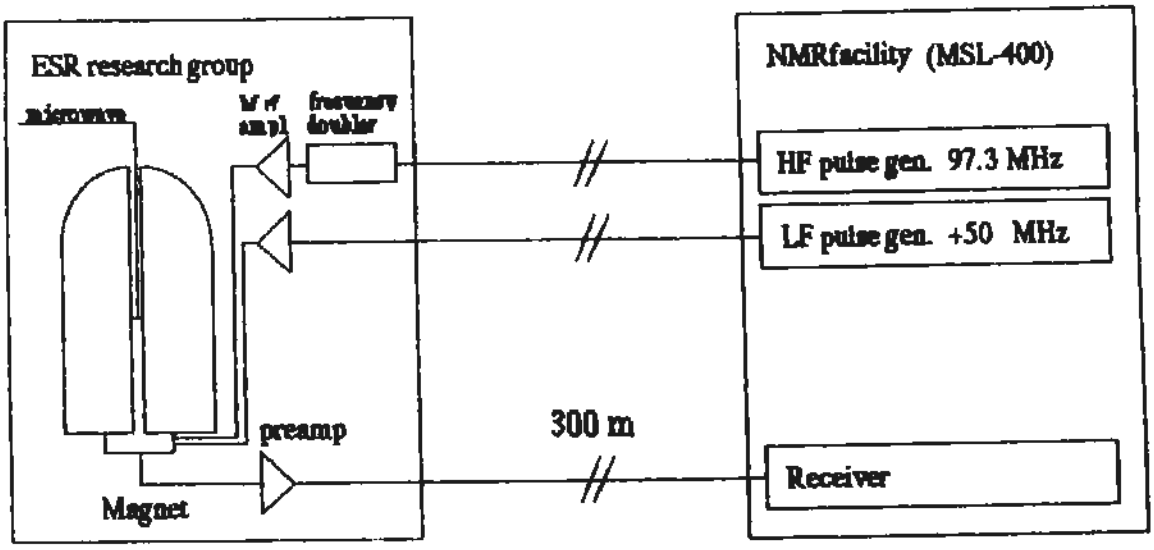
From Drs. C. Erkelens

Subject LONG DISTANCE NMR

Dear Dr. Shapiro,

Por a special project we needed to combine state of the art hr NMR and microwave equipment. This raised the problem of performing an experiment with two immobile instruments in different labs: The hr NMR equipment of the central NMR facility of our university in one building, and a high frequency microwave source with a magnet of the ESR research group in another building, at a distance of about 300 meters apart.

In order to achieve this without major investments we decided to set up "Long Distance NMR". We simply connected the two instruments with cables for signal transportation, purchased some low noise tuned NMR preamps, and installed the necessary high power RF amplifiers near the ESR magnet.



Schematic view of the "Long Distance NMR" set up

NMR frequency (^{1}H)	:	194.6 MHz
microwave frequency	:	128 GHz
attenuation by cables	:	15 dB

Since we needed to do ^{13}C NMR at 50 MHz and ^{1}H decoupling at 194.6 MHz, changing the frequency of the decoupler channel of the MSL-400 was necessary. Therefore we temporally connected the decoupler modulation to an external synthesizer. The installation is working well and the performance (signal to noise, pulse length) as good as can be obtained with a conventional set up.

In conclusion:

"Long Distance NMR" is a relatively easy inexpensive solution, whenever combination of NMR and other techniques involving major equipment (e.g. lasers) is desired.

C. Erkelens

D.J. van den Heuvel

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Department of Pure and Applied Chemistry

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PB/MAS

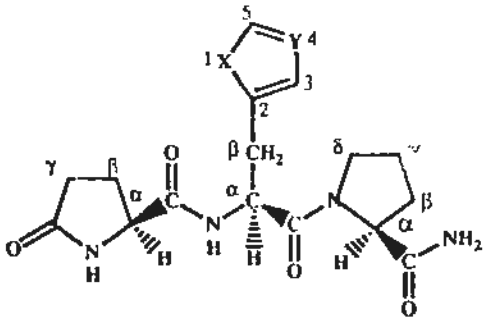
11th October, 1989 (received 11/1/89)

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

Dear Barry,

Proton and ^{13}C Spectra of some analogues of TRH

Over the years there have been many reports of synthesis of analogues of thyrotropin-releasing hormone (TRH) in which one of the amino-acid residues (usually the central histidine) has been replaced by non-natural residues. In connection with some work undertaken at the MRC Brain Metabolism Unit, Edinburgh, we had the occasion to run spectra of some of these sorts of compounds (see formulae). Here are the results of the proton and carbon spectra of four of them together with the results for TRH itself. The properties of the two diasterioisomeric pyrrolylalanine analogues were quite different (more than expected) and this difference is evident in their proton spectra.



TRH X=NH, Y=N

Thi^2-TRH X=S, Y=CH

Fur^2-TRH X=O, Y=CH

Pyr^2-TRH X=NH, Y=CH

Yours sincerely,

Peter Bladon

Christine Bladon

Christine Bladon (*)
* MRC Brain Metabolism Unit,
University Department of
Pharmacology,
1, George Sq., Edinburgh EH8 9JZ
Scotland, U.K.

Table 1 ^{1}H n.m.r. spectra (D_2O, ref. t-BuOH) of TRH analogues

	TRH	Thi^2-TRH (6)	Fur^2-TRH (7)	L-Pyr^2-TRH (8a)	D-Pyr^2-TRH (8b)
pGlu	Hα 4.29 (dd) J=8.9,4.8Hz	Hα 4.29 (dd) J=9.0,4.7Hz	Hα 4.29 (dd) J=9.0,4.7Hz	Hα 4.29 (dd) J=9.1,4.6Hz	Hα 4.29-4.36 (2H,m)
Xaa	H-5 7.70 (s) H-3 7.01 (s)	H-5 7.33 (dd) H-4 7.00 (m) H-3 J=4.8,1.5Hz	H-5 7.45 (d) H-4 6.39 (dd) H-3 6.25 (d) J=3.1,1.8Hz	H-5 6.79 (m) H-4 6.12 (m) H-3 6.05 (m)	H-5 6.78 (dd) H-4 6.12 (t) H-3 5.99 (m) J=3.2,1.5Hz
His ABX system	Hα 4.90 β H β' 3.08,2.99 J=7.2Hz				
Thi ABX system		Hα 4.94 β H β' 3.42,3.22 J=15.0,9.1,5.4Hz			
Fur ABX system			Hα 4.38 β H β' 3.20,3.05 J=15.2,8.9,5.5Hz		
Pyr ABX system				Hα 4.90 β H β' 3.13,3.04 J=15.4,7.6,7.3Hz	
Pyr ABX system					Hα approx.4.9 β H β' 2.99-3.12 (3H,m)
Pro	Hα 4.38 (dd) J=8.8, 4.9Hz δ H δ' 3.80 (m),3.54 (m)	Hα 4.39 (dd) J=8.5, 5.0Hz δ H δ' 3.83 (m),3.70 (m)	Hα 4,38 (dd) J=8.6,5.1Hz δ H δ' 3.82 (m),3.65 (m)	Hα 4.38 (dd) J=8.5,5.4Hz δ H δ' 3.78 (m),3.44 (m)	Hα 4.29-4.36 (2H,m) δ H δ' 3.74 (1H,m)

The ββ' and γγ' Pro and pGlu resonances occur as complex multiplets between 1.5 and 2.5 ppm.

Table 2 ^{13}C n.m.r. spectra (D_2O, ref.t-BuOH) of TRH analogues

	TRH$^+$	Thi^2-TRH (6)	Fur^2-TRH (7)	L-Pyr^2-TRH (8a)	D-Pyr^2-TRH (8b)
pGlu αCH	57.84	56.65	56.65	58.20	58.21
βCH_2	26.55	25.07	25.10	26.64	26.70
γCH_2	30.36	na	na	na	na
ring C=O	181.47	182.18	182.22	183.84	183.84
C=O	174.56	174.52	174.39	176.04	176.15
Xaa αCH	53.12	52.78	50.68	53.46	54.01
βCH_2	29.92	na	na	na	na
C-5	136.61	127.28	142.60	ca 120	119.77
C-4	-	127.07	110.65	109.01	109.49
C-3	nd	125.30	108.21		108.58
C-2	nd	138.13	150.20	127.63	127.46
C=O	172.34	170.81	170.89	173.08	173.45
Pro αCH	61.69	60.44	60.50	62.09	62.14
βCH_2	30.80	na	na	na	na
γCH_2	25.83	24.50	24.54	26.14	25.63
δCH_2	47.84	48.02	47.90	49.54	49.21
C=O	177.13	176.61	176.64	178.36	178.45
pGlu γCH_2		30.39	29.42	31.10	30.98
Xaa βCH_2		29.42	29.04	30.67	30.82
Pro βCH_2		28.99	28.92	30.16	30.32

* cis conformation resonances not included

+ run in CD_3OD

na = not unambiguously assigned

nd = not determined

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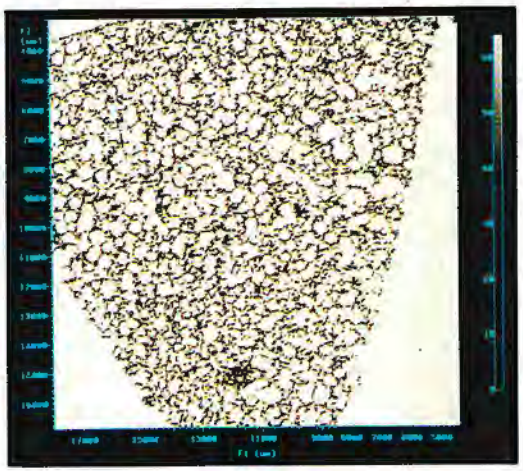
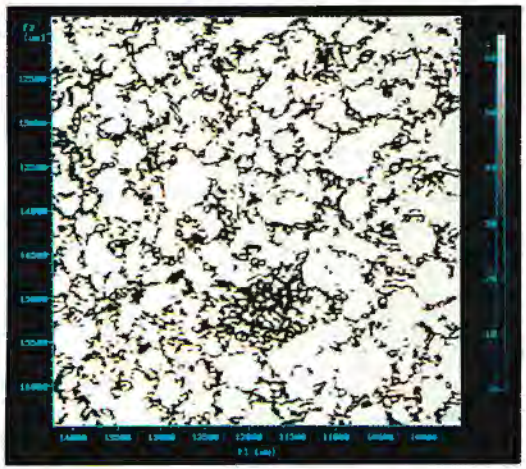
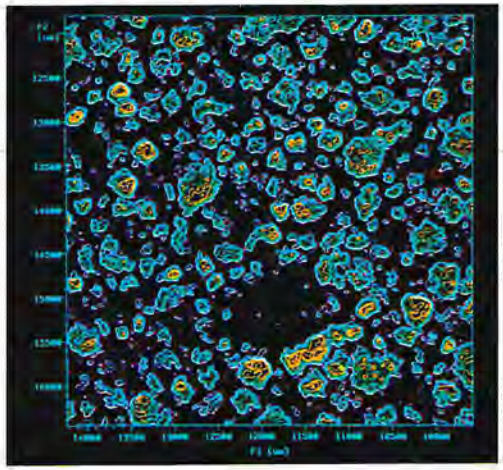
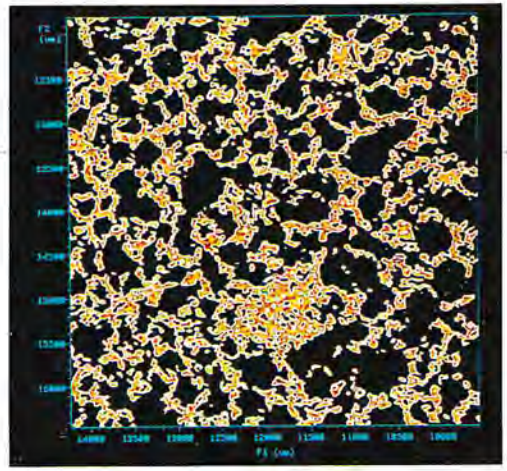
Run on a Varian UNITY-300 NMR Spectrometer, this PVA process-based sponge (courtesy of Prof. Dr. Gelan, Limburgs Universitair Centrum) demonstrates good water absorption properties in use. The images below were obtained with a T_e of 0.1 sec. The similarity in image contrast at two values of T_e (0.1 and 0.03 sec) demonstrates a high level of water mobility.

The structure of the sponge is cellular in nature with an average open structure size of 600 microns. The average cell wall thickness is 50 microns.



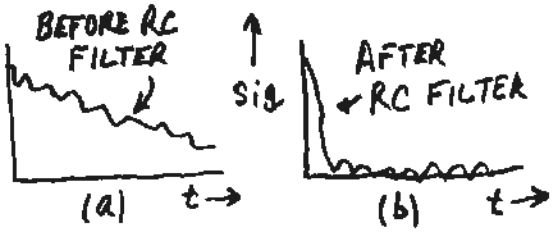






DYNAMIC RANGE, PHASE SHIFTERS, AND DIGITAL FILTERING

November 10, 1989 (received 11/17/89)
Brandeis University
Departments of Physics and of Biochemistry,
Waltham MA 02254 U. S. A.



Dear Barry:

Recently one of our probes was rebuilt by its maker (Craig Bradley). The sensitivity improved so much that we could no longer get the water signal low enough for optimum S/N. This and other frustrations led us to make some improvements on our custom-built system:

1. High pass filter and gain changer: Probably there are articles out there discussing use of a high-pass filter (such as a series C and parallel R to ground, passing frequencies above a hundred Hz or so) after the usual low pass (KHz range) filter and before the A/D converter, but I don't know of any. You might conceivably think such a filter would remove the residual water signal when you have the water frequency at the carrier frequency. The spectrum does look better close to water, but you still can't turn up the receiver gain any further because the filter converts the water signal step (Fig. A) to a sharper spike (Fig B) whose initial size is no smaller, and which overloads at the same level. However, combining this nearly worthless idea with an almost equally worthless one that Gupta and I published 18 years ago (Adv. Magn Res. vol. 5) gives a really useful improvement: The gain is decreased during the time of the spike of the signal in Fig. B, using a hardware "gain changer", and an exactly compensatory increase in gain is made by the software just after the data enters the computer. In initial tests the time constant RC of the filter is ½ millisec, the gain is changed by a factor of four usually for 2 millisec, and the increase in gain that is possible before overload is a factor of at least 10 db. The hardware is very simple-- fet's to change the gain; a preset counter to change the gain at the right time; and a shift register loaded by the computer, to load the counter. The A/D is preceded by a small amount of gain, after the gain changer, so that when the gain is set low the maximum filter output will still be able to saturate the A/D (which has an overload indicator and flag). We use this for proteins in the 20K range which have T2's of 10 to 20 millisecs, but even greater improvement would be possible with small molecules.

I consider this to be a simple and useful adjunct to accepted water elimination methods such as presaturation and selective pulsing, to make these methods a little easier. It is related to a paper by Davis et al (JMR 64 155 (1985)) but seems simpler. It also provides a way to investigate hard pulse spectroscopy in H_2O, since the ratio of 4 that we used might be increased to 64 or 128, by using a larger ratio of gain-change time to RC time constant. This seems unuseful to me because we don't work on small molecules where it would be feasible, and because I think there will be lots of non thermal noise associated with the water signal, due to amplifier gain and phase variation, and of course vibration.

2. Phase shifter based on Analog Devices AD9501 chips: We phase-shift a 6.15 MHz carrier which is then mixed with high frequencies to 500 MHz. The timer's clock is switched, from 1 MHz to 6.15/6 MHz, derived by dividing the 6.15 MHz carrier by 6, during any proton pulse so that gatings are in synchrony with the carrier, and we use two physically separate sets of phase

shifters. One set rotates the phase by multiples of 90, 45, and 30 degrees for changing the overall phases of composite pulses. The second set generates shifted carriers which are selected for individual parts of composite pulses such as JR pulses, and it includes a continuously variable shifter. This allows us to set up selective pulses independent of error in phase shifters. This system did not work well, perhaps because the phase shifters, based on one-shots, were unstable from pulse to pulse. Recently we built a new phase shifter system based on AD9501 delay chips, and found them excellent. The delay on the AD9501 is controlled by an 8 bit TTL input, but an external potentiometer can be and is used for a fine continuous delay. We first convert the TTL carrier square wave to 20 ns pulses using an edge detector, and then route these pulses through, or around, various fixed and variable shifters. There are six such delay chips in all, and the carrier is finally reconverted to a square wave whose length is determined by a seventh delay chip. This sounds complicated but it is very easy to wire these chips and they are not expensive.

3. Does 16 bits equal 16 bits? We have a 14 bit A/D converter, and wonder whether we should get a 16 bit one. The specs for many commercial 16 bit converters lists a ±.003% accuracy which is ± two, out of a 16 bit number, or a range of 4 (2 bits). In other words, those two bits don't do anything useful. Our 14 bit A/D lists the same .003% accuracy. You ought to ask your friend who sold you, or is trying to sell you, a half-million-dollar machine about the accuracy of its A/D, and how it is tested.

4. Oversampling: (What follows is not something we've done, it is purely an editorial.) There was a nice article by Delsuc and Lallemand (JMR 69, 504, (1986)), stating that dynamic range could be increased by oversampling. For example, if you sampled a 10 KHz wide FID at 160 KHz, you get a sixteen-fold (4 bit) increase in dynamic range. This would be a useful substitute for, or supplement to, your 16 (?) bit converter. The main problem with this is that you don't want to sling around data sets that are 16 times bigger than you now have. So you immediately think about digital filtering, to reduce the bandwidth 16-fold from 160 KHz to 10 KHz, and the number of points by the same factor; this is straightforward in principle. It so happens that we have a digital signal processing chip and board in my lab AT clone computer, that we now use for fast FFT, but that has fast I/O and incredible ability to digitally filter. We described our use of the board in another TAMU letter; it is based on a TI TMS320S25 chip, has 63 K x 16 addressable memory, and is made by Symmetric Research, 15 Central Way #9, Kirkland, WA 98033. They have just announced a board for the AT&T DSP32C that should be much faster. To make a long story short, these boards could take in data, sampled at a few hundred kHz, and spit out filtered data at a 10kHz rate, in real time and before it is seen by the main computer. Both cards cost less than $1600 with memory and assembler.

The joke is that this technology, which is more than a couple of years old, will allow us to eliminate those complicated audio filters that we all treasure, before our A/D, and replace them with a single filter, whose bandwidth can be anywhere between the NMR width and the high sampling rate. I wonder how many years it will be before we see the filters disappear on new machines?

Best wishes, al & Sara Al Redfield and Sara Kunz

Sandia National Laboratories

Albuquerque, New Mexico 87185

October 27, 1989
(received 11/3/89)

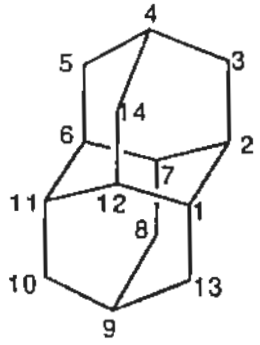
Prof. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

^{13}C Chemical Shifts of New Diamantanes: -SH and -NH_2 Derivatives

Dear Prof. Shapiro,

We have been interested in the structure of thin films -- Langmuir-Blodgett and "self-assembled" films -- of novel molecules as part of a project on optical and nonlinear optical materials. Systems based on diamantanes are of interest for several reasons including their rigid structure, their high symmetry, and the availabilty of many derivatives.

Correlations of the 13C chemical shifts of some diamantanes have previously been tabulated (H. Duddeck, F. Hollowood, A. Karim, M. A. McKervey, *J. C. S. Perkin II* **1979**, 361-365). In this letter, we would like to add chemical shifts of compounds which have recently been synthesized in our laboratories. The syntheses of these compounds will be reported elsewhere. Chemical shifts were assigned on the basis of relative intensities and chemical shift comparisons with published data on similarly substituted compounds.



Chemical shifts in ppm downfield from internal TMS (CDCl3)

4-NH2: (1,7,11) = 36.43; (2,6,12) = 39.05; (8,10,13) = 37.42; (3,5,14) = 46.71; (9) = 25.68; (4) = 45.91

4-SH : (1,7,11) = 35.98; (2,6,12) = 39.33; (8,10,13) = 37.41; (3,5,14) = 48.26; (9) = 25.517; (4) = 41.71

1-SH : (1) = 51.26; (2,12) = 39.35; (3,14) = 34.02; (4) = 25.56; (5) = 38.43; (6) = 36.50; (7,11) = 44.46; (8,10) = 37.77; (9) = 29.40; (13) = 50.07

1-NHAc: (1) = 56.05; (2,12) = 39.05; (3,14) = 32.75; (4) = 24.58; (5) = 38.05; (6) = 36.97; (7,11) = 38.70; (8,10) = 37.29; (9) = 28.58; (13) = 41.49

Sincerely yours,

Paul A. Cahill

Paul A. Cahill
Senior Member of Technical Staff
Chemistry of Organic Materials
Division 1811

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82-00540	Chloroform-d + 0.05% TMS (v/v)	99.8	100 g (5 x 100 g) (10 x 100 g)	20. 85. 165.
82-70001	Deuterium Oxide	99.9	100 g (5 x 100 g) (10 x 100 g) 1 kg	45. 210. 400. 385.
82-70901	Deuterium Oxide	99.8	**min.** 10 kg 25 kg	3500. 8500.
82-70002	Deuterium Oxide "100%"	99.96	10 g (5 x 10 g) 1 kg	15. 50. 550.
82-70003	Deuterium Oxide EXTRA	99.996	(10 x 0.75 mL) 10 g	50. 45.
84-70001	Deuterium-depleted Water	$< 5 \times 10^{-5}$	25 g (4 x 25 g) (10 x 25 g) (20 x 25 g) 1 kg	25. 85. 200. 300. 500.
82-00807	Dimethyl-d_6 Sulfoxide	99.9	(10 x 1 g) 10 g (50 x 1 g) (5 x 10 g) (100 x 1 g) (10 x 10 g)	14. 14. 65. 65. 125. 125.
82-00809	Dimethyl-d_6 Sulfoxide (multi-dose septum vials)	99.9	10 g (5 x 10 g) (10 x 10 g)	14. 65. 125.
82-00813	Dimethyl-d_6 Sulfoxide + 0.05% TMS (v/v)	99.9	25 g (5 x 25 g) 100 g	33. 155. 115.
82-00061	Methanol-d_4 (~0.7 atom % ^{13}C)	99.8	(10 x 1 g) 10 g (50 x 1 g) (5 x 10 g) (100 x 1 g) (10 x 10 g)	45. 45. 180. 180. 345. 345.
82-00059	Methanol-d_4 + 0.05% TMS (v/v) (~0.7 atom % ^{13}C)	99.8	10 g (5 x 10 g) (10 x 10 g) 25 g	45. 180. 345. 110.
82-86007	Nitrobenzene-d_5	99.5	10 g (5 x 10 g)	35. 150.
82-84081	Toluene-d_8	99.6	(10 x 1 g) 10 g (50 x 1 g) (5 x 10 g)	45. 45. 180. 180.
82-02510	Trifluoroacetic Acid-d	99.5	10 g (5 x 10 g) (10 x 10 g) 25 g	19. 80. 115. 40.

***PACKAGING:** Organic solvents (≤25 g) are sealed in glass ampoules to maintain the high quality of the solvents. Dimethyl-d_6 sulfoxide is also available in multi-dose septum vials. The waters (≤100 g), chloroform-d(≥100 g) and all solvents containing TMS or > 25 g are packaged in glass screw-cap bottles, except for the "100%" deuterium oxide (10 g), which is packaged in multi-dose septum vials. Deuterum oxide EXTRA is sealed in glass ampoules; deuterium oxide (≥1 kg) is packaged in plastic screw-cap bottles.

†Prices are FOB Miamisburg, OH for delivery in North America; please request prices for delivery to the other continents. **Minimum order, $50.**

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DEPARTMENT OF CHEMISTRY

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26 October, 1989
(received 11/4/89)

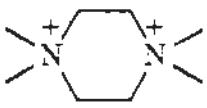
Dr. B. Shapiro
TAMU NMR Newsletter
966 Elsinor Court
PALO ALTO, CA 94303
U.S.A.

Dear Dr. Shapiro,

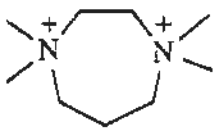
Exchanging Systems in Piperazines and Others

Here in Auckland we have made the jump from an FX60 to a Bruker AM400. (There are those who now believe everything is possible, solvable **and** instantaneous using NMR).

An early project was to look at some ^{14}N–^{13}C couplings in heterocycles containing quaternary N atoms. In the ^{13}C spectra at 15 MHz, the 2– and 3–bond couplings were barely resolved[1] and we decided to have a better look using the AM400. The first compound tried was the N,N,N′,N′ tetramethyl cation of piperazine, **1**.



1



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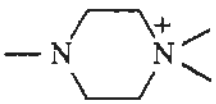

3

Imagine the initial consternation when our wonderful new spectrometer produced a ^{13}C spectrum with the methyl groups missing. It turns out that the cation is undergoing a cyclohexane-like chair-chair interconversion. The axial and equatorial methyl group ^{13}C signals have a coalescence temperature of 300K and the room temperature spectra showed a very broad hump buried in the baseline noise.

We have now investigated a series of these cations, varying the alkyl substituent and ring size, eg. **2**, as well as allowing rapid N inversion in disubstituted cations such as **3**. Variable temperature studies of the ^{1}H and ^{13}C spectra in a variety of solvents have let us calculate $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the chair-chair interconversions in these compounds. Some representative data are given in the Table.

We don't observe the ^{15}N J couplings very well at the higher field except well above room temperature. Effectively, the difference in exchange regimes means the AM400 apparently operates at about 30°C below that of the FX60.

Having become interested in exchanging systems, we have also been looking at chemical exchange in borates[2], polymolybdates[3], tin halides[4] and gallium halides. For example, the Ga-73 spectra of mixed aqueous solutions of $GaCl_4^-$ and $GaBr_4^-$ show one peak due to rapid ligand exchange. An ether extract of such a solution displays 5 signals from each of the complex acids $H^+(aq)[GaCl_nBr_{4-n}]$ (n = 0–4). The exchange rate is very much slower in the less polar ether solvent. We see similar behaviour in the tin(II) halides, but only on cooling to 213 K.

Please credit this contribution to Roger Meder at the Forest Research Institute, Rotorua.

Yours sincerely

J.M. Coddington M.J. Taylor

References:

1. M.J. Taylor, D.J. Calvert and C.M. Hobbis, *Magn. Reson. Chem.*, **26**, 619-629 (1988).
2. J.M. Coddington and M.J. Taylor, *J. Coord. Chem.*, **20**, 27-38 (1989).
3. J.M. Coddington and M.J. Taylor, *J. Chem. Soc., Dalton Trans.*, (1989) *in press*.
4. J.M. Coddington and M.J. Taylor, *J. Chem. Soc., Dalton Trans.*, (1989) *in press*.

Table: Chair-Chair Interconversions

Cation	Solvent	Monitoring Nucleus	Δν (Hz)	T_c (K)	Inversion Rate (Hz)	ΔG^* (kJ mol^{-1})
1	D_2O	^{13}C of CH_3	845	300	1877	54.7
	CD_3CN	^{13}C of CH_3	840	297	1866	54.1
	CD_3CN	^{1}H of CH_3	47	272	105	55.9
2	D_2O	^{13}C of CH_3	430	300	955	56.4
	CD_3CN	^{13}C of CH_3	438	302	973	56.7
	CD_3CN	^{1}H of ring CH_2	95	288	214	57.6
	CD_3CN	^{1}H of CH_3	26	280	58	59.0
3	D_2O	^{13}C of CH_3	970	294	2155	53.2
	CD_3CN	^{13}C of CH_3	985	283	2188	51.1
	CD_3CN	^{1}H of ring CH_2	120	266	267	52.6
	CD_3CN	^{1}H of CH_3	40	258	90	53.4

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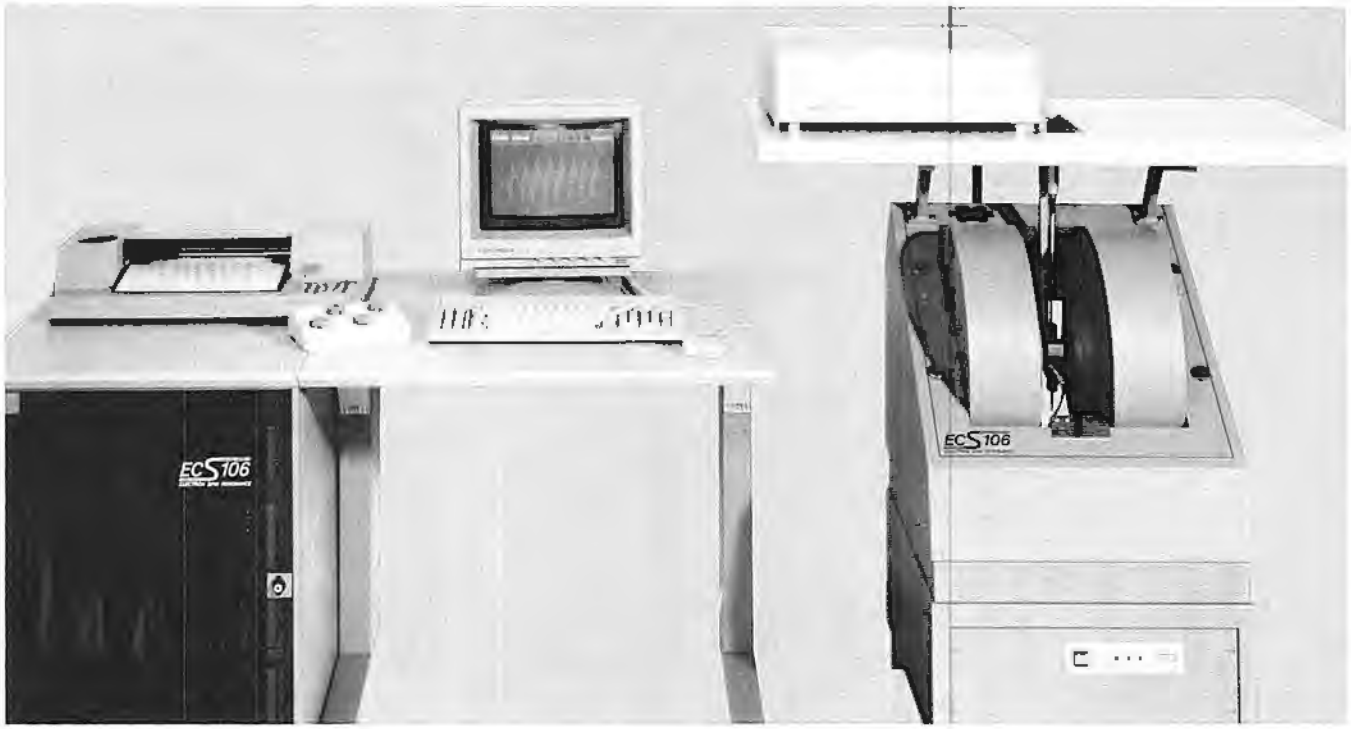

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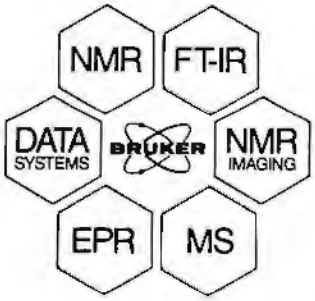
For information contact Dr. A. Heiss, Bruker Instruments, Inc., Manning Park, Billerica, MA 01821, (508) 663-7406.



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October 16, 1989
(received 11/3/89)

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

Dear Dr. Shapiro:

RE: CROSS POLARIZATION EXPERIMENTS ON A BRUKER MSL SPECTROMETER USING THE "NEW-STYLE" FIFTH CHANNEL MODULATOR

I would like to inform your readers of some results that were obtained recently by Bob Taylor, Bruker Applications Scientist, and myself regarding improved capabilities for the fifth channel modulator on MSL spectrometers. The fifth channel modulator on the MSL provides continuously variable phase (0 - 360 deg) and amplitude control (0 -100%) as an alternative to the normal +/-X, +/-Y four phase modulator. Hardware improvements in the "new style" fifth channel have phase and amplitude switching times reduced to less than 2 usec. However, the modifications to the process controller compiler (PCCOM 890701) that are required to implement cross-polarization using the fifth channel have only recently become available.

An abbreviated listing of a standard cross-polarization pulse program is given below in which the amplitudes on the irradiation channel (F2) during the 90 degree proton pulse, the spin-lock duration (contact time) and the decoupling duration can be controlled independently. This is the first implementation of such a sequence that we are aware of. With PCCOM versions prior to 890701, this program could not be correctly compiled because of the simultaneous pulses indicated in D5. The amplitude variation that is obtained on the modulator output is modified by the Bruker power amplifiers which are non-linear. Ideally, linear amplifiers are recommended for this application; however, the Bruker amplifiers are adequate over a limited range of amplitude variation and power levels.

The pulse program reflects some of the current restrictions that are inherent in PCCOM 890701. The most important of these is that in the durations where the observe (F1) and irradiation (F2) transmitters are on simultaneously and the F2 phase is controlled by the fifth channel, a phase list cannot be used for the F1 pulse. This limitation was circumvented by replicating the basic sequence four times and explicitly varying the F1 phase.

```
; CPCYCL5.PC
; CROSS POLARIZATION PULSE SEQUENCE WITH PHASE ALTERNATION
; F2 FIFTH CHANNEL PHASE 278 CORRESPONDS TO -Y
; AMPLITUDE 38 WITH DP=OH CORRESPONDS TO FULL OUTPUT W/ DP=3H
; VD MINIMUM 1.35U

PROT XT

START,  2U
 LOOP 2 TIMES
        D11     [F2 @PLS1 RGATE]            ; H1 90 DEGREE +-
        VD                                  ; VARIABLE DELAY
        D5      [F2 (278/38) F1 +X RGATE]   ; CONTACT PULSE
        D3      [SV2 (278/38) GV2 RGATE]    ; DEAD TIME DELAY
        D4      [SV2 (278/38) GV2 STA]      ; D3+D4=2*DW
        D7      [SV2 (278/38) GV2]          ; USE NT FOR ACQUISITION
        DO      [RGATE]                     ; RECYCLE DELAY
        1M      [++PLS1]
     END LOOP
        2U

        D5      [F2 (278/38) F1 +Y RGATE]

        D5      [F2 (278/38) F1 -X RGATE]

        D5      [F2 (278/38) F1 -Y RGATE]

 GOTO START

BEGIN LISTS
PLS1,   +X -X
;PLS2,   +X +X +Y +Y -X -X -Y -Y
RLS,    +X -X +Y -Y -X +X -Y +Y
END LISTS

; RECEIVER MODE : RPN
; TRIGGER MODE  : NT
; DECOUPLER MODE: OO
; NS=8*N
```

In this particular sequence where the proton 90 degree pulse and the spin-lock pulse are controlled by the normal phase modulator and the fifth channel modulator, respectively, the phase shifts for the fifth channel modulator must be calibrated with respect to the normal modulator. This was accomplished by using a simple modification of the DECTEST.PC program in which the -Y pulse was substituted with a fifth channel pulse whose phase was varied in the foreground by the use of an additive constant.

Please credit this contribution to the Hercules account.

Sincerely,

Mark J. Sullivan
Senior Research Chemist

/MJS
6725U

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November 9, 1989
(received 11/15/89)

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

Dear Barry,

Rites of passage are always formidable experiences. Our first step hesitates with trepidation as we become initiated into the TAMU newsletter society and face the terror of contribution reminders. Perhaps the best way to start is to dust off some old research and give it a different shine:

The oxygenation status is a key parameter of cellular function. Conventional tissue measurements of oxygen rely on arterial-venous differences in hemoglobin (Hb) saturation or on substrate levels, such as lactate/pyruvate, which are sensitive to oxygenation changes. Electrochemical and optical techniques have also been used. These extant techniques, however, are invasive or yield a spatially averaged measurement in vivo. Both the invasive manipulations and the imprecise tissue localization can pose difficulties in studying the effect of tissue oxygen levels under normal and pathophysiological conditions.

Monitoring the 1H NMR signal of myoglobin (Mb) is a way to observe non-invasively and precisely the cellular oxygenation status in local tissue regions. Myoglobin is a well characterized intracellular protein that plays an important role in storing oxygen and in facilitating O2 diffusion in the cell. Under deoxygenation conditions, the heme iron in Mb is paramagnetic (S=2). The hyperfine interaction shifts the proximal NH resonance to approximately 80 ppm,. where the lipid and other metabolite signals do not appear. Substantial model compound and protein studies have assigned definitively this peak to the proximal histidyl NH (1). Under oxygenation conditions, the heme iron is diamagnetic (S=0) and the hyperfine interaction disappears. Correspondingly the unencumbered signal intensity of the proximal histidyl NH resonance at 80 ppm decreases with oxygenation. The resonance is therefore a distinct marker of intracellular oxygenation.

Fig. 1 displays perfused heart spectra between 100 and 50 ppm. Reference 1H NMR spectra were collected while the heart was perfused with oxygenated buffer, reflected in fig. 1a. Each spectrum required four minutes of signal accumulation. During perfusion with oxygenated buffer, no signals appeared in this spectral region. After four reference spectra, the perfusion line was clamped to create global ischemia. A signal then appeared, fig. 1b, at 79 ppm, in excellent agreement with the assignment of the proximal histidine NH signal of deoxy Mb (1). Five spectra were collected during the ischemia period and showed a persistent signal at 79 ppm. No other signal appeared in this region. To confirm the assignment and to monitor the response of the signal to oxygen ligation, the heart was recirculated with oxygenated perfusate. The Mb signal disappeared with reoxygenation, shown in fig. 1c. During the reoxygenation period, no signal at 79 ppm was detected.

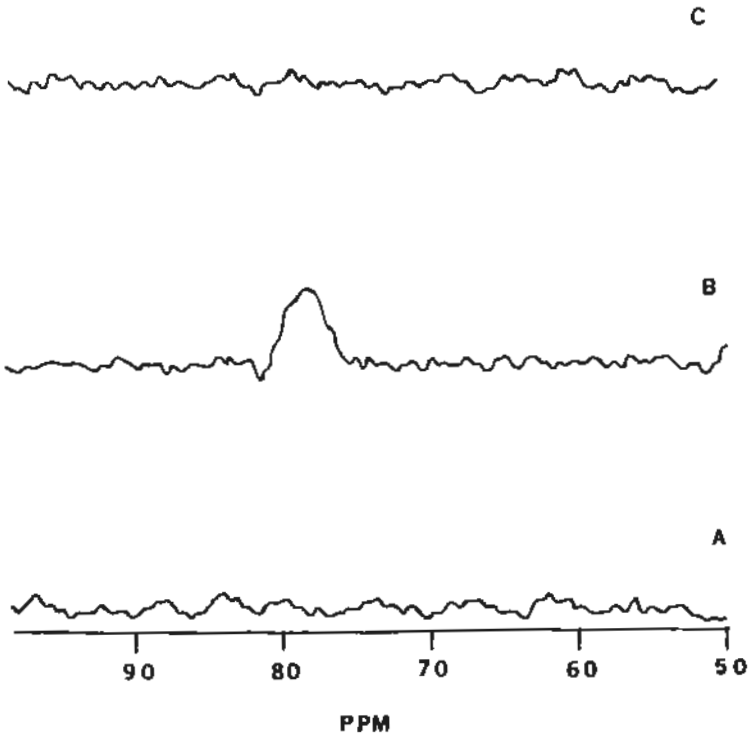
Clearly the 1H NMR signal of deoxy Mb is detectable in heart and responds to oxygen tension. Optical spectral analysis of the perfusate indicates no contribution from any extracellular Mb. Its visibility is consistent with a previous study on excised muscle (2). Coupled with spatial localization techniques, the strategy to measure tissue oxygenation with the myoglobin signal will permit us to take different steps in understanding the role of oxygen in regulating cellular function.

Sincerely,

Thomas Jue
Biological Chemistry

Steve Anderson
Human Physiology

1. G. N. La Mar, D. L. Budd, and H. Goff, BBRC, 77, 104 (1977).
2. D. Livingston, G., N. La Mar, and W. D. Brown, Science 220, 71 (1983).



Fremont Magnetic Resonance
3315 Seldon Court
Fremont CA 94539
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System Noise Meters

When an NMR spectrometer experiences a loss in sensitivity, the operator is faced with the task of determining the cause. A lower signal-to-noise ratio arises from either a loss of signal from decreasing probe performance or an increase in noise from the console electronics. The systematic approach to solving this common problem is to separate and isolate the variables which influence the NMR instrument's sensitivity. This is often a difficult task because an NMR system consists of individual modules, any one of which can become the limiting factor in the performance of the overall system. The NMR operator needs tools and methods for independently determining the performance of the individual modules.

Identifying Sources of Electronic Noise

Measuring the system noise figure is a straightforward method of isolating each of the variables in an NMR system's performance. The system noise figure is a measure of how much noise is being added to the NMR spectrum by the console electronics, relative to a "perfect" console. It can be thought of as a measure of the "Quality" of the NMR system's electronic performance. Few NMR spectroscopists have taken advantage of noise figure measurements because the procedure was confusing, noise meter devices were expensive and/or results were not reproducible. FMR offers an inexpensive Noise Meter Kit which makes system noise figure measurements quick, easy and reproducible. An RF shielded noise source is connected in place of the probe and the meter is calibrated with the noise source at room temperature. The noise source is then cooled in liquid nitrogen and the system noise figure is read directly off the meter. The entire process takes less than 5 minutes. Exchanging preamplifiers, filters, trans couplers, directional couplers, etc. and repeating the tests, directly informs the operator about how these devices affect the NMR instrument's performance. The meter can be used to determine if and how much noise is coming from the system's power amplifiers by simply monitoring the noise level while connecting and disconnecting the power amplifier. If amplifier noise is leaking into the system, the meter reading will increase when the amplifier is connected. Once the system's baseline performance has been determined, any loss in sensitivity which appears can quickly be traced to its source. The time saved in diagnosing problems will more than balance the cost of the Noise Meter Kit. The Noise Meter Kit comes with complete instructions and is in stock for immediate delivery.

Noise Meter Kit $500.00

Probe Repairs and Upgrades

Improving Probe Performance

Once the console's performance has been determined, the NMR operator can turn attention to probe performance. Many existing probes have substantially lower sensitivity than new probes. This is due to availability of better quality components and improved design of probes and/or to the degradation over time of the existing probe by oxidation or contamination of the coil and capacitors. These existing probes can be restored to their original performance or completely upgraded to a performance comparable to newly designed probes. And this can be done for much less than a new probe. Some older designs can often have sensitivity improved by 50 to 200%.

To help you improve probe performance, FMR offers:

- Probe repairs at reasonable parts plus labor costs.
- Probe upgrades for existing probes (even to different insert size and/or nucleus) for much less than a new probe.
- New standard and customized probes at competitive price and performance.

Water Suppression

Does your probe have trouble with water suppression? This can often arise from either having the probe coil's leads pickup signal or from too long of a receiver coil or both. FMR can modify your current probe to help eliminate these problems.

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Instrumentation Note 14

Baseline Problems ??

The more information a spectroscopist tries to extract from a spectrum, the more important a non-distorted (straight) baseline becomes. Examples of areas where baseline distortion creates unwanted difficulties are:

- Small signals in the presence of larger signals.
- Spectral integration.
- Difference Spectra.
- Water Saturation.
- 2DFT.

In some cases, "baseline distortion" can arise from real NMR signals. Broad signals, which can be wider than the observation sweep width, create "distortion". Examples of this are probe background, wide-line ^{2}H spectra of solids or ^{31}P surface coil spectra. When these special cases of "real signal" are identified and eliminated from the discussion, there are still many cases where instrumentally induced baseline distortion complicates data interpretation. Examples of sources of these instrumental baseline distortions are:

- Digitizer overload (Clipping).
- Preamp and/or receiver overload.
- Audio filters.
- Some RF stage's slow recovery from overload.
- Probe acoustical ringing.

These are difficult problems to diagnose and often more than one problem is present at a time. The approach is to isolate each variable as much as possible and repair or replace the offending module or find a work-around solution. An easy one to find and eliminate is clipping of the digitizer. Every spectroscopist knows how to detect and eliminate this one, but let's use it as an example of a particular type of baseline distortion which arises from "overloading". Using a simple sample such as Ethyl Benzene while observing protons, when the digitizer is not overloaded, the spectrum has a normal straight baseline. If the signal amplitude is increased to the point where the first few points of the FID are clipped, the signals will appear to sit in a shallow "hole" in the baseline. The more the signal is clipped, the deeper the hole.

Other areas of the spectrometer's receiver can "clip" or overload besides the digitizer. When there is too much signal for an amplifier or mixer to handle and remain in its linear range, the high amplitude areas of the FID are suppressed relative to the low amplitude areas. This creates an amplifier "clip" which results in a baseline distortion similar to digitizer clipping. Another problem with this type of overload is the creation of "extra" peaks in the spectrum by intermodulation mixing of signals from the probe. For the simple case of two strong signals in the spectrum with this type of overloading, the two signals will mix to yield sum and difference signals as well as the main signals. This can be easy to see with wide sweep widths when the signals are confined to a small region near the center of the spectrum. In other cases it is more confusing since the signals can "foldback" from outside the spectral window and not appear to be either a sum or a difference. But for this discussion, the main area to notice is the shallow well around the peaks. This type of RF overload occurs most easily when running strong samples such as proteins in water. Very slight RF or digitizer overload has been used to create a very slight "hole" around the residual water signal to reduce the water "tail" in water saturation experiments.

Another type of baseline distortion arises from the distortion of the first few points of an FID. This can come from probe acoustical ringing or, more commonly, filter distortion. If the first few points of the FID are distorted, then during the mathematical processes of Fourier Transform and phase correction a baseline roll is introduced. When there is one large signal (water) in the spectrum, it's small distortion leads to a very curved baseline when examined at the amplitude of most of the interesting spectral peaks.

To minimize this problem, it is best to use a good Butterworth filter set at least 50% wider than the acquired spectrum. A Bessel filter has a better impulse response and produces even less distortion but with it's more gradual rolloff there is a slight reduction in signal to noise.

Either with the proper audio filter or without, a reduction in the baseline curvature can be obtained by adjusting the time between the end of the pulse and the digitizer trigger (DE in Bruker, GE and Nicolet terms) such that the B (first order) phase correction is near zero. For an FID with a distorted first point, this will reduce the mathematical outcome of phasing to a DC offset of the baseline, which is easier to correct. If the digitizer does sequential, rather than simultaneous, data acquisition for each channel during quadrature detection (some Brukers), the transmitter phase also needs to be adjusted to give an A (zero order) phase correction near zero to achieve a similar result.

GE NMR Instruments

General Electric Company
P O Box 4905, Fremont, CA 94539

November 8, 1989
(received 11/10/89)

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

Temblor Resistant NMR

Dear Dr. Shapiro:

Although selection of coherence using B_o field gradients was introduced several years ago (1,2), a dearth of subsequent high resolution applications appears to be a result of limits in gradient technology. The recent introduction of fast actively shielded gradients (3) has made it possible to take advantage of the significant benefits of gradient coherence selection and to devise gradient enhanced versions of the many useful 1D and multidimensional homonuclear and heteronuclear nmr experiments. Our initial efforts were focused on in vivo applications in which gradient selection of double quantum coherence was used to obtain spectra and images of metabolites such as lactate (4,5).

A Major advantage of these methods is that since only the desired coherences are selectively rephased, phase cycling and, in some cases, traditional water suppression methods are not required.

In the example shown here, a double quantum cosy spectrum of sucrose in H_2O is obtained using the gradient enhanced experiment (ge_2qcosy) shown in Figure 1. Only a single acquisition per evolution time is required to select the +1/+2 coherence pathway. The large population of water protons remain dephased, thus avoiding loss of signal which can result from misuse of presaturation, selective excitation and/or attenuation. The receiver never detects this unwanted signal, while desired coherences, even from resonances at the solvent chemical shift, are observed in an optimum way.

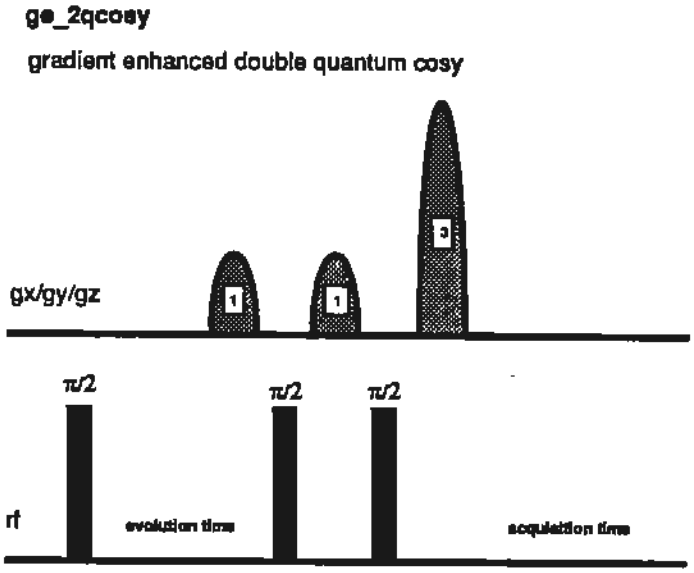

Figure 1

One of the most important features of this approach is that it avoids using a difference to select double quantum coherence and hence significantly reduces the sensitivity of the method to motion. Last month, the effect of vibration on this experiment was unexpectedly tested. A ge_2qcosy spectrum of sucrose in water (Figure 2) was obtained as a 1K by 512 matrix with a single acquisition per evolution increment. This 13 minute run was started at about 5:00 p.m. in the afternoon on the 17th of October and was subjected to an unusually high level of vibration mid-run. The data were processed late the next day. Water suppression remained acceptable (not detected) and only a moderate amount of peak distortion was observed.

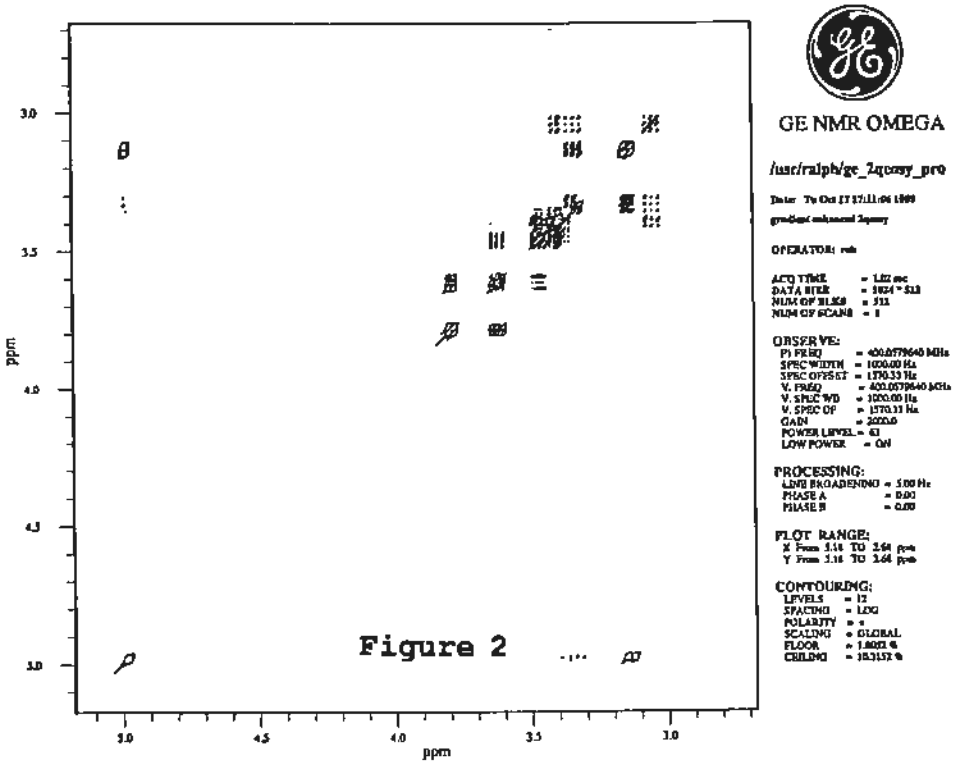

Figure 2

Although successful, we do not recommend that this vibration test be duplicated in your laboratory.

Best regards,

Ralph E. Hurd
Manager, Applications
GE NMR Instruments

References

1. A.A. Maudsley, A. Wokaun and R.R. Ernst, *Chem. Phys. Lett. 55*, 9 (1978).
2. A. Bax, P.G. De Jong, A. F. Mehlkopf and J. Smidt, *Chem. Phys. Lett. 69*, 567-570 (1980).
3. P.B. Roemer, W.A. Edelstein and J.S. Hickey, Fifth Annual Meeting of the Society of Magnetic Resonance in Medicine, Montreal 1986, Abstracts, p. 1067.
4. C.H. Sotak, D.M. Freeman and R.E. Hurd, *J. Magn. Reson.* 78, 355-361 (1988).
5. R.E. Hurd and D. M. Freeman, *PNAS* 86, 4402-4406, 1989.

Dr. V. Wray

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Biotechnologische
Forschung mbH

Molekulare
Strukturforschung

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

Ihre Zeichen / Your ref.	Ihr Schreiben vom / Your message of	Unsere Zeichen / Our ref.	Datum / Date
			19. October 1989 (received 10/24/89)

Protein Design and NMR

Dear Dr. Shapiro,

Protein Design has now assumed a particularly important role in biotechnology. In keeping with this our institute has established a research group which is involved with all aspects of molecular modelling and structure elucidation of peptides and proteins. As a backup to our X-ray crystallography group and to get additional insight into 3D structures in solution, we have now initiated NMR investigations of various peptides and proteins. Although our first experiences using our old 400 MHz instrument were not too fruitful the work has been greatly aided by the installation of a Bruker AM 600 spectrometer earlier this year. We are pleased with the performance of this instrument; not only have we seen a large increase in sensitivity but the ability to perform all the modern 2D techniques has greatly simplified structure determination both for large and small molecules. For the former our efforts have been concentrated on the structure elucidation of a 56-residue protein which has been modelled here in the Genetics Department as a potential inhibitor of human elastase and whose structure has been solved by our X-ray group.

A second topic was the NMR investigation of an amphiphilic helix-peptide designed by Dr. R. Moser at the University of Zürich. As 10 out of a total of 26 residues are leucines and 10 others are of the "long side chain" type (2 Arg, 2 Lys, 4 Glu, 2 Gln), the spin system assignment was quite difficult. However this was considerably simplified by the use of a "Clean TOCSY" experiment (C. Griesinger at al., J. Am. Chem. Soc. 1988, 110, 7870) as shown in the attached figure. Cross peaks between the NH's and methyl groups of the 10 leucines could be immediately assigned together with the very helpful correlations between the NH's and protons of the long side chain amino acids. Although there is considerable overlap of signals 121 nOe's were unambiguously determined and incorporated into the GROMOS 87 program package on our VAX computer. Various starting structures resulted in an alpha helical configuration of the peptide. This rather satisfying result gives added encouragement for further research in this type of design work. A paper is in preparation.

Yours sincerely,

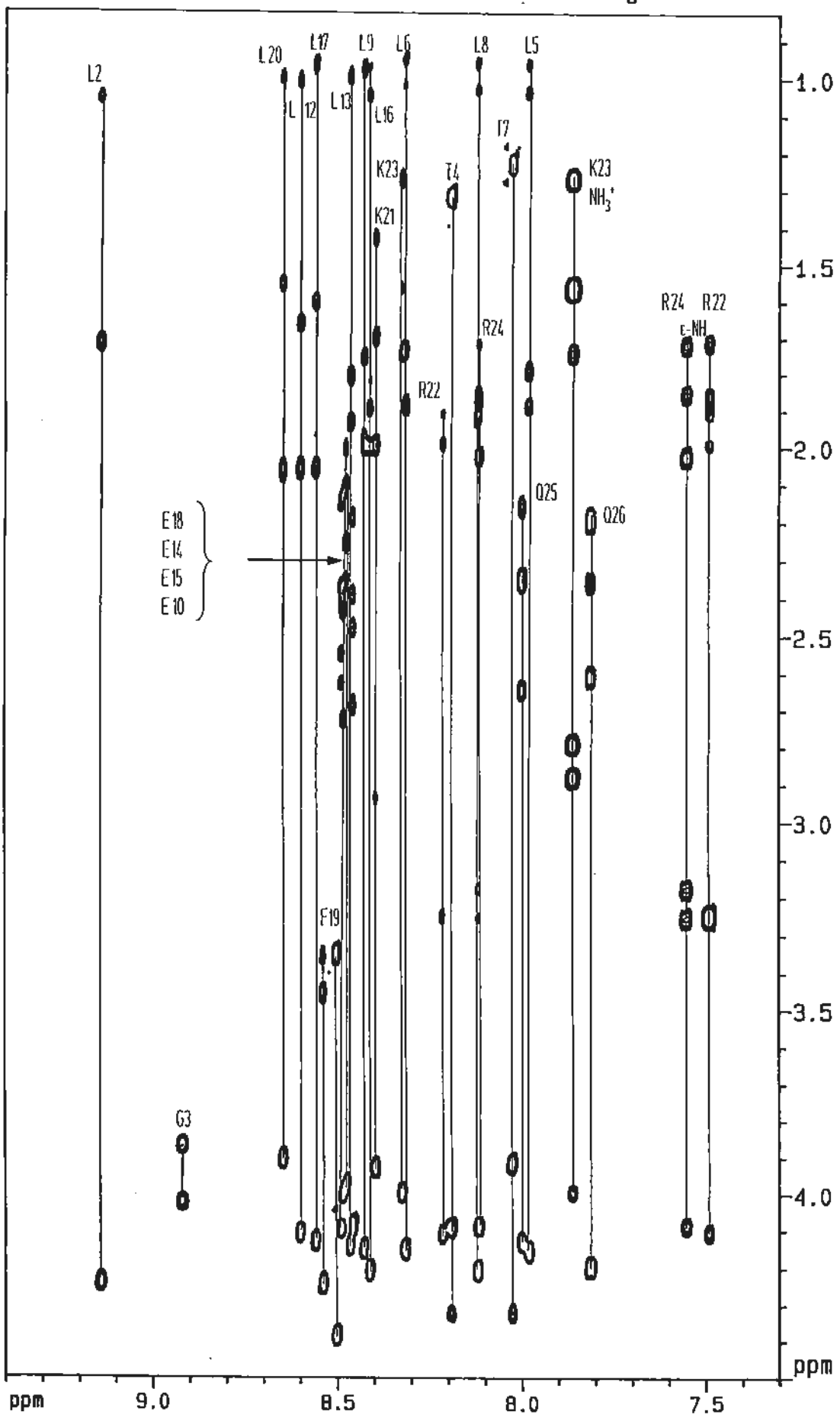
Werner Klaus

Werner Klaus

Victor Wray

Victor Wray

Clean TOCSY (mixing time 100.2 ms) for a 4.5 mM solution of the 26 amino acid peptide dissolved in CD_3OH at 290°K



NMRi
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– Press Release –

November 13, 1989, Syracuse, NY. The Digital Design group of Paris, France, announces today the acquisition of a majority equity interest in New Methods Research, Inc. (NMRi). Digital Design acquired its interest in the Syracuse high-technology firm to complement existing product lines and to utilize distribution channels of the Digital Design group.

NMRi is a leading developer of advanced computer software for nuclear magnetic resonance (NMR) spectroscopy, an instrumental method for chemical and biochemical analysis, and magnetic resonance imaging (MRI). The company also designs and configures laboratory computer networks for its clients in North America, Europe, and Japan.

The Digital Design group, with operating affiliates in Germany, Spain and Italy, as well as the USA and headquarters in France, will provide NMRi with an effective European base for sales and customer support.

Together, NMRi and Digital Design will develop a new generation of software and computer workstation products. The capital invested by Digital Design will also be used to enhance NMRi's new products for image analysis and molecular structure determination from NMR spectra and computation.

Digital Design, S.A. was founded in 1981 by Jean-Marie Lucani, who still heads the group as President and Chief Executive Officer. The company has two main business lines – design and production of image processing systems and distribution of mass memory computer peripherals. New Methods Research, Inc., was founded in 1983 by George C. Levy, Science and Technology Professor at Syracuse University. NMRi will continue to operate under Peter E. Kent, President, who joined the company in early 1988. Professor Levy will continue to be Chairman of NMRi's Board of Directors.

Digital Design was advised and assisted by Banexi International, the merchant banking affiliate of the Banque Nationale de Paris.

Contacts:

Digital Design Inc.
Jean-Marie Lucani
3060 Business Park Drive
Norcross, Georgia 30071
404-447-0274
FAX 404-263-0405

New Methods Research, Inc.
Peter E. Kent
719 E. Genesee Street
Syracuse, New York 13210
315-424-0329
FAX 315-424-0356

SEASONS GREETINGS FROM NMRi

* * * * *

All of us at New Methods Research, would like to wish everyone in the NMR community, a safe and happy holiday season.

Université de Nancy I

Laboratoire de Méthodologie RMN

November 2,1989
(received 11/7/89)

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

Subject: SUFIR pulse program for an ASPECT 3000

Dear Professor Shapiro,

We have just been called out for the implementation of the SUFIR (SUper Fast Inversion-Recovery) (1) pulse sequence on BRUKER spectrometers operating with an ASPECT 3000 computer. Originally, this experiment has been devised for a modified BRUKER WP 200 interfaced to a Nicolet 1180 computer permitting in an easy way to alternatively acquire the two subsequences, (90°)(Acq) and (180°-τ-90°)(Acq) in separate memory blocks with an accurate timing. This "one-shot" T_1 determination takes a measuring time comparable to that of a single-pulse experiment and numerous checks have demonstrated its reliability. It may be also useful for the quick and precise recognition of the relaxation time scale prior to any elaborated NMR experiment. You will find enclosed a listing of the pulse program and the automation sequence prepared for an ASPECT 3000 operating under DISMSL 87 software.

Sincerely yours,

P. Tekely K. Elbayed D. Canet

(1) D. Canet, J. Brondeau, and K. Elbayed, *J. Magn. Reson.* 77, 483 (1988)

B.P. 239 - 54506 VANDŒUVRE-LES-NANCY Cedex (France) - Tél. 8 ~~528.93.93~~ 83912049
Unité Associée au C.N.R.S. n° 406 - Laboratoire d'Etude des Solutions Organiques et Colloïdales

```
------ FILE: SUFIR   .PC

;SUFIR.PC
;SUPERFAST T1 DETERMINATION BY INVERSION-RECOVERY
; SEE CANET ET AL., J.M.R. 77, (1988), 483
DE=DW*5/4
START,    D1  [F1 +X RGATE]
          DE  [STA RGATE]
          VD                        ; TAU MUST BE 0.5T1-3T1; VD LIST
          D2  [F1 +X RGATE]         ; PI PULSE
          VD
          D1  [F1 +X RGATE]
          DE  [STA RGATE]
          VD
       LOOP C1 TIMES                ; C1=16*N
          D1  [F1 PLS1^ RGATE]      ; PI/2 PULSE
          D1  [F1 PLS2^ RGATE]      ; PI/2 PULSE
          D1  [F1 PLS3^ RGATE]      ; PI/2 PULSE
          DE  [STA RGATE]
          VD
          D1  [F1 PLS4^ RGATE]      ; PI/2 PULSE
          D3  [F1 PLS5^ RGATE]      ; 4PI/3 PULSE
          D1  [F1 PLS6^ RGATE]      ; PI/2 PULSE
          VD
          D1  [F1 PLS7^ RGATE]      ; PI/2 PULSE
          D1  [F1 PLS8^ RGATE]      ; PI/2 PULSE
          D1  [F1 PLS9^ RGATE]      ; PI/2 PULSE
          DE  [STA RGATE]
          VD
       END LOOP
GOTO START
BEGIN LISTS
PLS1, +X +X +X +X +X +X +X +X
PLS2, +Y +Y +Y +Y +Y +Y +Y +Y
PLS3, -Y -Y -Y -Y +Y +Y +Y +Y
PLS4, +X +Y +Y +X +X +Y +Y +X
PLS5, +Y -X -X +Y +Y -X -X +Y
PLS6, +X +Y +Y +X +X +Y +Y +X
PLS7, +X +X +X +X +X +X +X +X
PLS8, +Y +Y +Y +Y +Y +Y +Y +Y
PLS9, -Y -Y -Y -Y +Y +Y +Y +Y
RLS,  +X +X +X +X +X +X +X +X
END LISTS
;DS=2
;NR=C1-NUMBER OF REPETITIONS= NUMBER OF TIMES THE LOOP IS EXECUTED
;NI=2- BUFFERED ACQUISITION
;NS=1
;OPF
;RPN- LOADED BY RP
;NE=NUMBER OF TAU VALUES IN VD LIST

------ FILE: SUFIR

1 ZE
2 VD
3 GO
4 RE #3 ;MUST BE CALLED FIDn.SER WHERE n IS THE JOB NUMBER
5 WR #1
6 IF #1
7 IF #3
8 RE #3
9 WR #2
10 IF #2
11 RF #3.001
12 IN=1
13 EXIT
```

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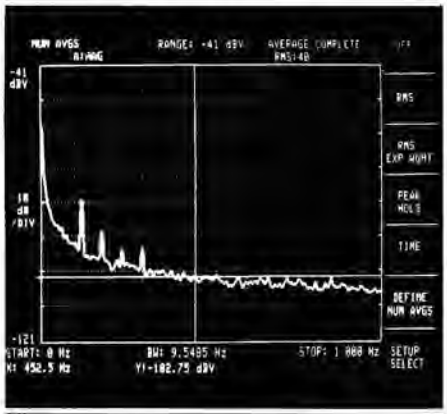

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October 31 (Halloween), 1989
(received 11/6/89)

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

Dear Barry,

NMR pulsed gradient diffusion has emerged as a quick and simple technique for measuring self diffusion coefficients of fluids. This technique has been shown to be useful for probing the structures of ordered fluids such as surfactant solutions, microemulsions and polymer solutions. The structures found in many of these systems are temperature dependent, thus requiring temperature control in the NMR probe. Most commercial spectrometers control the sample temperature using a stream of temperature regulated air fed in through the bottom of the probe. When the temperature of the air is much above room temperature, the air cools as it ascends, creating temperature gradients along the axis of the sample tube. This effect is illustrated in the first figure where the ^{59}Co resonance halfwidth has been used to estimate the temperature grandient s along a $Co(CN)_6$ sample using various cooling air flow rates. The ^{59}Co resonace of this compound is known to have a strong temperature dependence of its chemical shift (about 1.40 ppm/^{o}C). That the observed broadening of the resonance is due to thermal gradients along the tube axis was checked by repeating the same experiment on a 2 mm NMR sample tube.

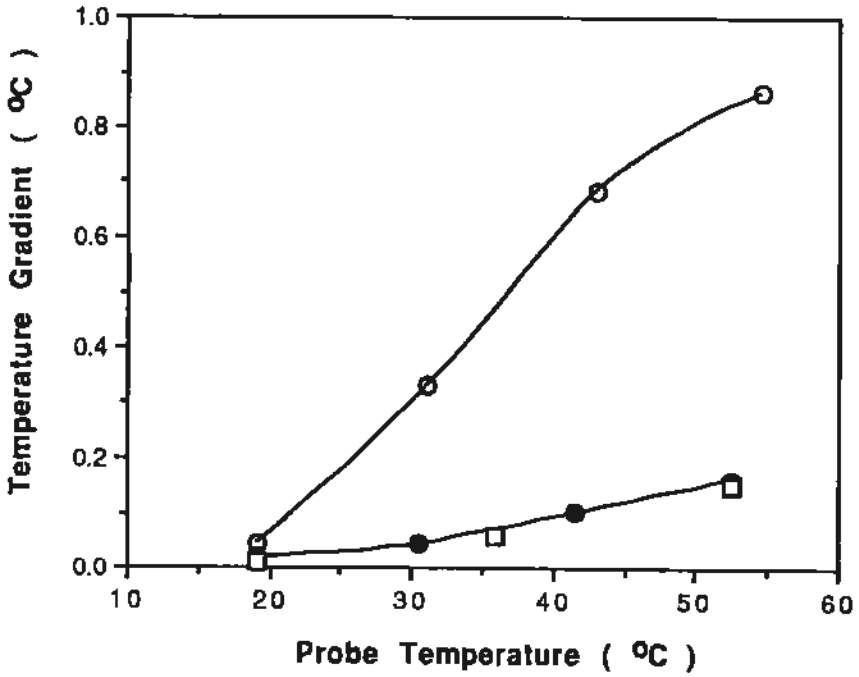

Fig. 2: Calculated temperature gradients as a function of measured probe temperature. Experiments were carried out using 5 mm O. D. sample tubes and a cooling air flow rate of 9 LPM (o), 5 mm O. D. sample tubes and a cooling air flow rate of 17 LPM (●), and 2 mm O. D. sample tubes and a cooling air flow rate of 17 LPM (□). Notice that reducing the sample tube diameter does not effect the linewidth of the ^{59}Co signal.

One of the effects of a temperature gradient is to create differences in solvent density along the sample tube axis. If the temperature gradient is large enough, the stabilizing effects of viscosity and thermal conductivity are overcome by destabilizing buoyancy and thermal, or Rayleigh-Benard, convection ensues. Critical Rayleigh numbers, determining the onset of convective flow, have been calculated analytically, assuming cylindrical geometries and various diameter to length ratios . One of the general conclusions of these studies is that the critical Rayleigh number should increase as the diameter of the cylinder decreases and the sample viscosity increases, i.e.. convection is harder to establish for viscose samples in narrower sample tubes. Hence, the onset of convection may be postponed by decreasing the temperature gradient in the sample, increasing sample viscosity or decreasing the diameter of the sample tube. Figure 2 shows the ratio of the self-diffusion coefficients measured on an H_2O sample using the NMR PFG method to the diffusion coefficient measured using radioisotope tracer method vs. measured probe temperature. We find that even with increased cooling air flow rates the onset of convective flow brings about large positive errors in self-diffusion coefficients measured using the NMR method. However, as predicted by the theory, decreasing the sample tube diameter or increasing the sample viscosity help prevent these errors, presumably by preventing the onset of convection.

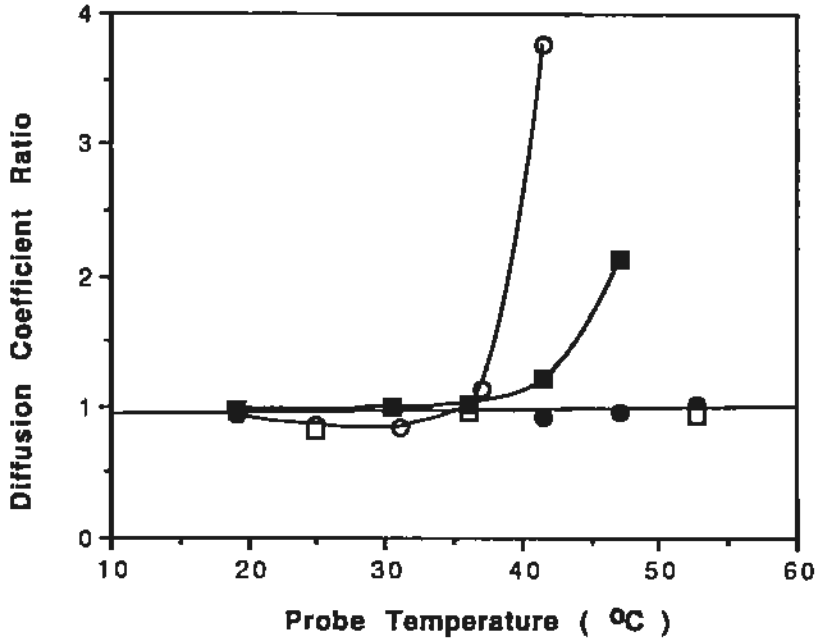

Fig. 4: Experiments were carried out on deionize water samples using a 5 mm O. D. sample tube and a 9 LPM cooling air flow rate (o), a 5 mm O. D. sample tube and a 17 LPM air flow rate (■) and a 2 mm O. D. sample tube and a 17 LPM air flow rate (●). A final experiment measured self-diffusion coefficients of a water sample containing 600 ppm xanthan biopolymer using a 5 mm O. D. sample tube and a cooling air flow rate of 17 LPM (□).

Sincerely Yours,

Warren J. Goux
Associate Professor of Chemistry

National Research Council Canada
Conseil national de recherches Canada

Division of Biological Sciences
Division des sciences biologiques

Ottawa, Canada
K1A 0R6

November 10, 1989
(received 11/12/89)

Prof. B.L. Shapiro
966 Elsinore Court
Palo Alto, California 94303
USA

PROBE MELTDOWN

Dear professor Shapiro,

On our AM-200, about 50% of overnight runs are done at high temperature (70 C). One morning the sample was found to be carbonized and the plastic cap on the tube had melted. Irreparable damages to the 5 mm dual probe and melted solder joints in the shim assembly had also occurred. A malfunction in the VT-100 was the cause of the problem. TH1 (s.c.r.) in the heater power circuit had shorted. Heater power went up uncontrolled until the regulation fuse blew, but not before serious damage was done.

Although such a malfunction is very rare, to prevent any further costly incidents, modifications to the safety circuit of the VT-100 were made. On one side of TR3 (transformer) in the power supply board there is a relay which is switched on when the heater power is turned on. This relay can be turned off when overheating occurs, even if the scr's are shorted. The control to the relay will be provided by a Newport 268 digital thermometer (Tschudin & Bax, TAMU NMR 354-62) with option 05/06 added. This option permits a digital setpoint, latched operation and front panel reset button. The alarm output from the Newport will be used to control the actuating coil of the relay. The alarm temperature will be hard wired in the 05/06 option. More detail will be furnished if requested.

Sincerely,

A Simard
André Simard

R B Holmes
Randy Holmes

J R Brisson
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November 9, 1989
(received 11/13/89)

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

RE: More on Rare Functional Groups in Wood Pulps.

Dear Dr. Shapiro:

Our latest object of scrutiny is carboxyl group content in cellulosic pulps. While this is measured historically by ion-exchange or conductometric titration, the result simply measures numbers of titratable groups, whether they be carboxylic acids or other species. Further, these procedures miss entirely on groups which are not noticeably acidic but may still be of interest (e.g., enols arising from oxidative bleaching).

We are investigating $^{13}CH_2N_2$ treatment as an alternative. A bleached pulp, methylated heterogeneously in ether suspension, exhibits large CP/MAS signals at 60-63 δ with smaller ones at 54 and 52 δ; these are all $-OCH_3$ resonances. Gentle alkaline hydrolysis of the methylated pulp eliminates the 54 δ peak entirely and reduces the 60-63 δ intensity. Intensity calculations and consideration of the difference spectrum (showing what was removed by hydrolysis) produce a carboxyl result in good agreement with the titration result (29 vs. 35 meq/kg), assuming that the 54 δ peak is the methyl ester ^{13}C.

More interesting to us are the methyl groups at 60-63 δ, as these constitute some 10-20 times the carboxyl result. Our not-yet iron-clad interpretation is that these are methyl ethers of enol groups, formed by enolization of cyclic ketones in the cellulose polymer. Support is offered by ascorbic acid which methylates at both enediol oxygens under similar heterogeneous conditions, giving $-OCH_3$ peaks at 59 δ in D_2O. Another possibility is that some normal carbohydrate hydroxyls are methylated, probably in the more accessible hemicellulose fraction of the pulp; methylcellulose contains methyl signals in this region. We are continuing with model compounds and fractionated pulps to sort this out -- enol contents of the magnitude indicated defy conventional wisdom in wood chemistry.

Warmest regards,

Larry Amos

Larry Amos
Weyerhaeuser Analytical Services

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Rolf G. Tschudin
Engineer, NMR Section
DHHS/NIH/LCP
Bldg. 2, Rm. B2-02
Bethesda, Maryland 20892
(301) 496 2692

13. November, 89
(received 11/14/89)

GARP IN A BOX.

Dear Barry

The GARP1 Decoupling Sequence* has become very popular in our laboratory since it appears to be more effective than previous modulation schemes. To simplify the setup and execution, we have liberated it from the instrument console and put it in a box. (Block diagram Fig. 1.).

A dial allows the timing to be set to 90° values from 20 to 999 us. A switch selects between random or coherent starts of the sequence. The output is TTL, or RF through a 180° switch at low level (10 dbm). Switching between CW and BB can be done via 1 line (gate) or 2 lines (on/off).

Any one interested in a detailed schematic or hardware please drop me a line.

Best regards

Rolf

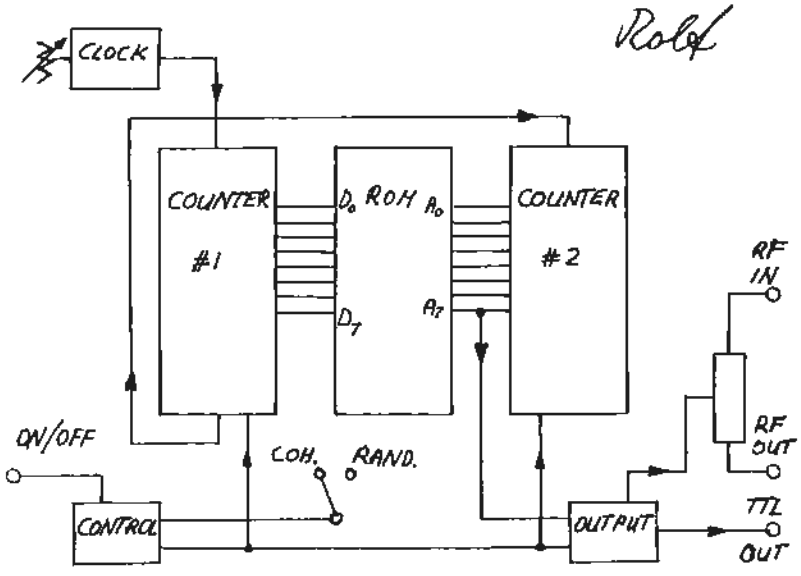

Fig. 1

* A.J.Shaka, P.B.Barker and Ray Freeman,
J. Magn. Reson. 64, 547 (1985)

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To: Dr. B.L. Shapiro
TAMU Newsletter
966 Elsinore Court
Palo Alto, CA 94303

afd. dept. ref. no.

onderw. re. doorkiesnummer in-dialling datum. date

Subject: Automatic shimming for *in vivo* MR spectroscopy.

Best, October 27, 1989
(received 11/13/89)

Dear Dr. Shapiro,

Everybody involved in MR knows how important the magnetic field homogeneity is for spectral resolution. This also holds for *in vivo* spectroscopy. Since shimming must be done prior to every examination and because in most cases it is done manually it is time consuming and requires a lot of experience from the operator. This makes shimming a critical step in the routine clinical application of MR spectroscopy.
In order to overcome this problem we developed an automatic shimming method which is capable of optimizing the field homogeneity in a fast and reliable way, independent of the skills of the operator.

The optimization procedure [1] uses the integral of the magnitude time domain signal of the tissue water as a homogeneity criterion.
The program can either optimize on the magnitude signal or on the normalised magnitude signal.

$$J = \frac{\sum_{i=1}^{i=n} |x_i|}{|x_1|} \tag{1}$$

In this equation x_1 through x_i represent the complex samples of the MR time signal, the so called FID.
Data point x_1 is the first maximum the software encounters in the modulus representation of the time signal. By dividing all data points by the value of this breakpoint the total integral is normalised.
In case of strong fluctuations in the time signal e.g. due to motion artifacts the absolute value of the FID integral can be used. The absolute value is simply calculated by

$$J = \sum_{i=1}^{i=n} |x_i| \tag{2}$$

For each shim coil the optimum of the FID signal is determined in the following way:
Starting at an initial value I_0 a first step is taken towards a new current I_1. Subsequently, as long as the maximum is not encountered the step size is doubled. As soon as the maximum of the FID integral is passed the search direction is reversed and the step size is decreased. In this way the program iterates towards an optimum for every shimchannel resulting in an optimal field homogeneity over the defined volume.

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telefax. +3140762205

The technique is now successfully used during patient and volunteer studies. Starting e.g. from a standard shimsetting, 7 shimcurrents (X, Y, Z, ZX, ZY, XY, and X^2-Y^2) are adjusted to optimize the field homogeneity over the selected region of interest. On average for a 100 - 200 cc volume of the human brain the method achieves a water line width (FWHM) ranging from 0.1 to 0.03 ppm. in about 5 minutes. Also in human liver and heart studies the technique has been applied with success. The figure shows an example of a water-suppressed ^{1}H NMR spectrum taken from a volume located in the brain of a healthy volunteer after shimming with the FID optimization procedure. The excellent shimming is confirmed by the fact that metabolites can easily be detected up to 4 ppm. We think that with the FID optimization algorithm we have found a good and reliable method for automatic optimization of the magnetic field homogeneity for *in vivo* human spectroscopy. Moreover the results obtained with this method exceed any result obtained with manual shimming, both in time required and in achieved homogeneity.

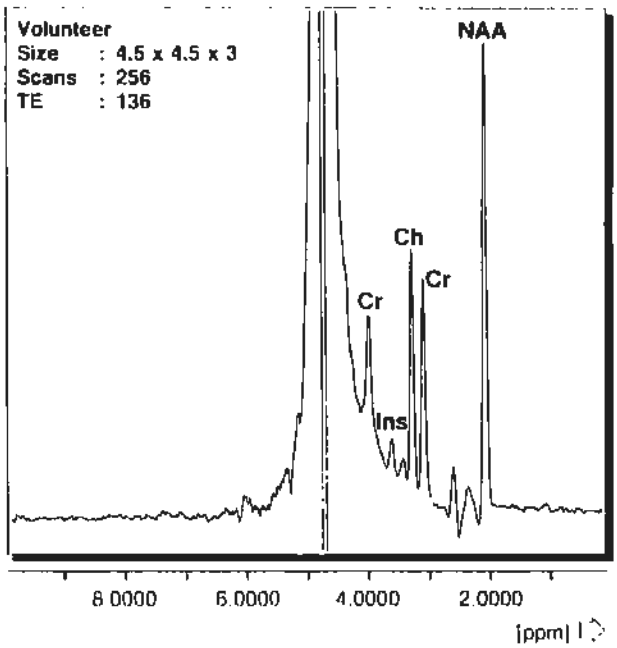
[1] Holz, D., *et al*, Med. Phys. **15**, 898 (1988)

Please credit this contribution to Dr. Joost A.B. Lohman's account.

Yours sincerely,

Jan W.A.H. Vermeulen

Ad J. H. Mariën



Water suppressed ^{1}H spectrum obtained, after automatic shimming, from a 60 cc volume located in the human brain. From left to right the resonances of Creatine (N-CH_2), Inositols (H4, H6), Taurine (N-CH_2, S-CH_2), Choline (N-$(CH_3)_3$), Creatine (N-CH_3), N-Acetyl aspartate (β-CH_2), Glutamine/Glutamate (γ-CH_2) and N-Acetyl aspartate (CH_3).

375-62

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Dr. B.L. Shapiro
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PALO ALTO, CA 94303
U.S.A.

Your reference and date	Our reference	Office telephone	Date
	JAP/mk/703	(015) 78 5892	02-11-1989 (received 11/14/89)

Subject
^{17}O NMR study of the solvation of Dysprosium(III) ions in solutions of Dysprosium chloride in methanol and ethylene glycol

Sub-division
Department of Organic Chemistry

Dear Dr. Shapiro,

Previously, we have observed that, for paramagnetic lanthanides, the contact contribution to the Ln(III)-induced shift of a Ln(III)-bound ^{17}O nucleus is almost independent of the nature of the concerning ligand.[1] Therefore, Ln(III)-induced ^{17}O shifts can be utilized to establish the oxygen coordination sites of a ligand and to determine the stoichiometry of the complex. For Dy(III) as the lanthanide, the induced shift is dominated by the contact shift and a laborious dissection into the contact and pseudocontact contributions is not needed.
We now have applied this method to study the solvation of Dy(III) in solutions of $DyCl_3.6H_2O$ in methanol and ethylene glycol. The exchange of ^{17}O between bound and free ligands was fast on the NMR time scale. Straight lines were obtained in plots of the ^{17}O chemical shifts versus the molar ratio Dy(III)/ligand (ρ, $\rho <$ 0.1, correlation coefficients > 0.999). The induced ^{17}O shifts extrapolated to $\rho = 1$ correspond to $n\Delta$, where n is the number of Dy(III)-bound oxygens of the concerning ligand and Δ is the bound shift of that oxygen nucleus. We know from a study of Dy(III)-induced shifts of D_2O that Δ = -2267 ppm at 30 °C. Therefore, division of the observed induced shifts extrapolated to $\rho = 1$ by -2267 gives n. The values of n obtained are:

CD_3OD	6
$HOCH_2CH_2OH$	9

Thus, Dy(III) is coordinated by only 6 methanol ligands. The first coordination sphere of Dy(III) is completed by 3 Cl^- ions, which is in agreement with various literature reports based on a.o. ^{139}La and ^{35}Cl NMR.[2] In ethylene glycol the Cl^- ions are, however, expelled from the first coordination sphere.

Yours sincerely,

Chen Zhi Chen Zhi

J.A. Peters

References
1. J.A. Peters and A.P.G. Kieboom, Recl. Trav. Chim. Pays-Bas 102, 381 (1983).

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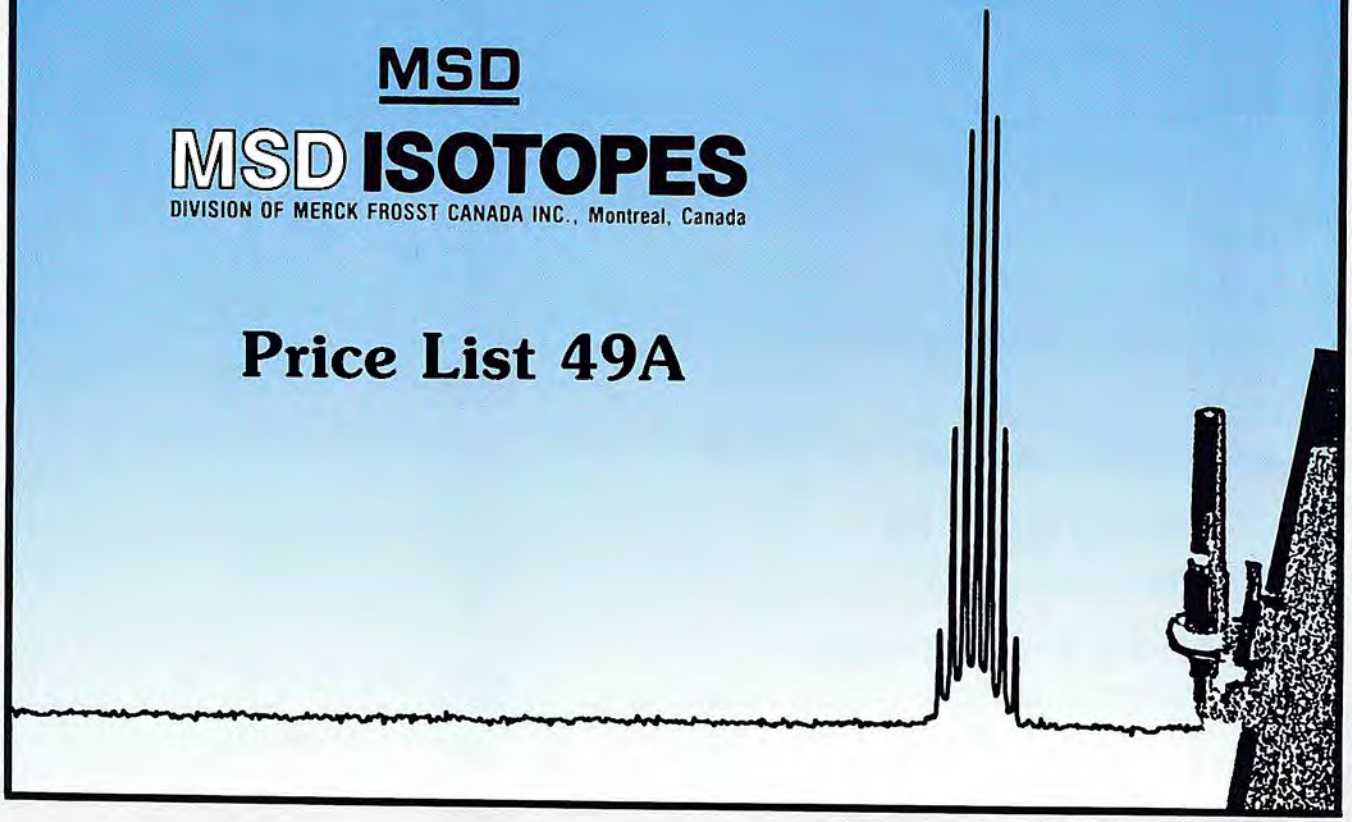

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Dr B L Shapiro
TAMU NMR Newsletter
966 Elsmore Court
Palo Alto
CA 94303
USA

10th November 1989
(received 11/16/89)

Dear Barry

IN SEARCH OF THE LOST RESONANCE
(OR CLOSE ENCOUNTERS OF THE SECOND-ORDER)

Many years ago I looked at the effect of two (^{13}C, ^{14}N) residual dipolar couplings on one ^{13}C (1,2). In each case, the ^{13}C NMR signal was split into quartets, the magnitude of which depends on the quadrupolar and dipolar parameters and the relative orientation of the quadrupolar and dipolar tensors. Recently, this effect has been observed for two (^{119}Sn, ^{35}Cl) residual dipolar couplings convoluted with the effect of J-couplings in ^{119}Sn MAS NMR (3).

To test further the effect of two residual dipolar couplings, I chose urea as an ideal sample for a ^{13}C study. Urea has only one carbon species present and this carbon is between two amine groups with identical quadrupolar and dipolar tensors. In this case a 1:1:4 triplet is expected. As the T_1 was long (~2 mins) and the $T_{1\rho}$ did not decay over 0.5s of spin-lock, multiple contact 25 MHz ^{13}C CPMAS NMR was used. However, no signal was observed.

Recently, I purchased a 99.8% enriched ^{13}C-urea sample from MSD Istopes. The spectrum shown in the figure corresponds to about seven years of averaging on a natural abundance sample on our Bruker MSL 100. Not all the signal appears to be present. A ^{13}C spin counting experiment only saw 55% of the signal on our MSL 300. The splitting is simulated using a program based on that of Opella et al (4) to χ = -3.41 MHz, η = 0.31 (5), $\alpha^D = \beta^D = 90°$. Not only is the total integrated intensity low, but there appears to be an incorrect intensity pattern for the multiplet, the centre component being the most intense.

cont.../

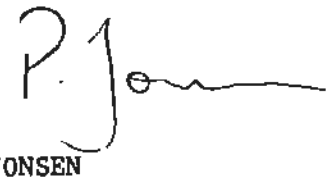
Dr B L Shapiro
TAMU NMR Newsletter

10th November 1989

We attribute these observations to the possibility of an orientationally anisotropic ^{14}N T_1 (6), which gives three orientation regimes: (a) fully self-decoupled residual dipolar coupling (intensity at the centre of the multiplet); (b) unaffected residual dipolar coupling (1:4:4 triplet); (c) intermediate ^{14}N T_1s (lost intensity). I would be interested to hear from any readers who have any other ideas!

A more complete account of this work is currently being submitted to J. Magn. Reson.

Yours sincerely,



DR P JONSEN
Spectroscopy Branch

Please credit this account to BP Research.

(1) R K Harris, P Jonsen, K J Packer, Magn. Reson. Chem., 23, 565-577 (1985).

(2) R K Harris, P Jonsen, K J Packer, Magn. Reson. Chem., 24, 977-983 (1986).

(3) D C Apperley, B Haiping, R K Harris, personal communication (1989).

(4) S J Opella, J G Hexem, M H Frey, T A Cross, Phil. Trans. R. Soc. London, Ser. A, 299, 665 (1981).

(5) C T O'Konski, K Tonzuka, J. Chem. Phys. 51, 461-463 (1969).

(6) A Zussman, J. Chem. Phys., 58, 1514-1522 (1971).

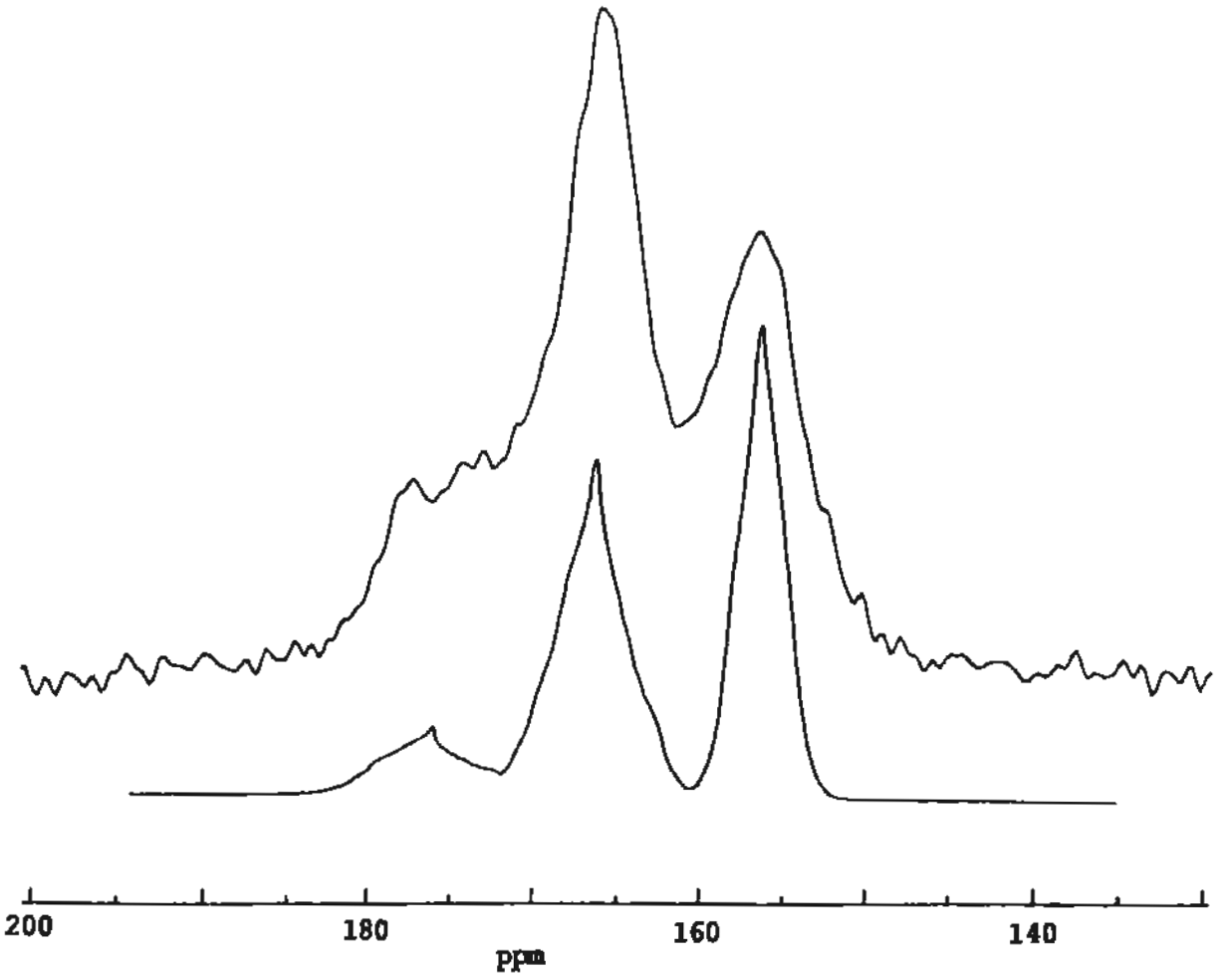


FIGURE 25.2 MHz ^{13}C CPMAS NMR spectrum of 99.8% enriched ^{13}C-urea. Recycle delay of 60s was used (with flip-back) and 352 accumulations. The simulation has not been artificially broadened.

375-68

Philip H Bolton

Department of Chemistry **Wesleyan University** **Middletown, Connecticut 06457**
phone 203 344 8544 x-2539 **fax 203 344 7960**

14 November 1989

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Bernard L. Shapiro, Editor
TAMU NMR Newsletter
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DEPARTMENT OF CHEMISTRY

FH

The Interdisciplinary Center for Biotechnology Research of the University of Florida will sponsor a workshop on NMR and Structure of Biomolecules to be held in Gainesville, March 4-9, 1990. The workshop will include lectures by leaders in the field of protein and carbohydrate chemistry, with Kurt Wüthrich as the leadoff speaker. Participants will have opportunity to work with hardware and software such as that appropriate in the use of NOE results to assist in the modeling of large molecules. Lectures will be directed both toward of spectroscopists who wish to learn about biological applications of NMR and toward biochemists and biotechnologists who are interested in how NMR can be applied to solution of their problems of molecular structure, conformation, and interactions. Information about the workshop is available from W. S. Brey, Department of Chemistry, University of Florida, Gainesville FL 32611-2046, phone (904) 392-0520.

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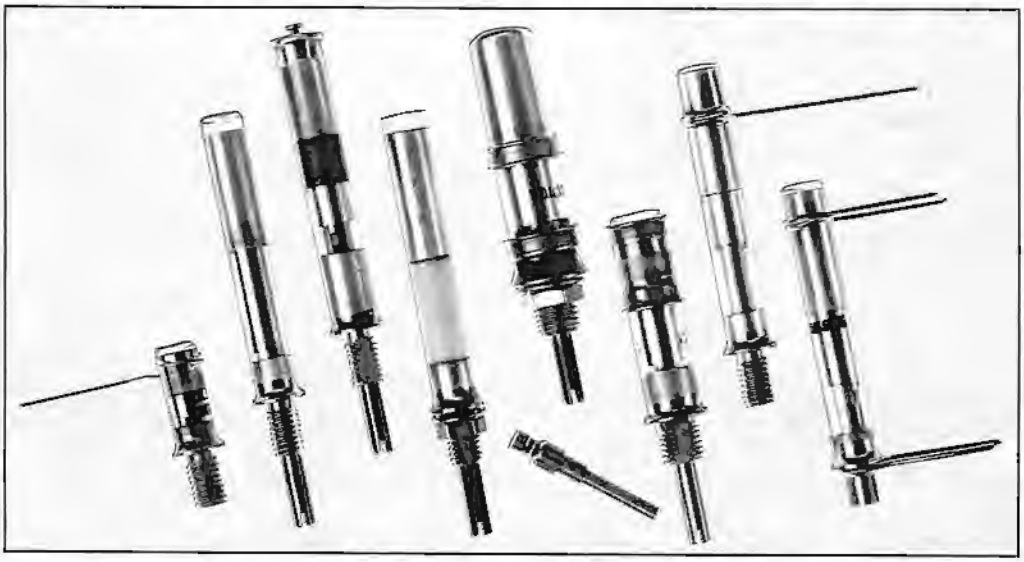

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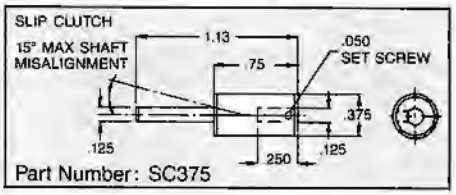

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October 20th, 1989
(received 11/15/89)

Dr. B.L. Shapiro
TAMU NMR NEWSLETTER
966 Elsinore Court
Palo Alto, CA 94303
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Dear Dr. Shapiro,

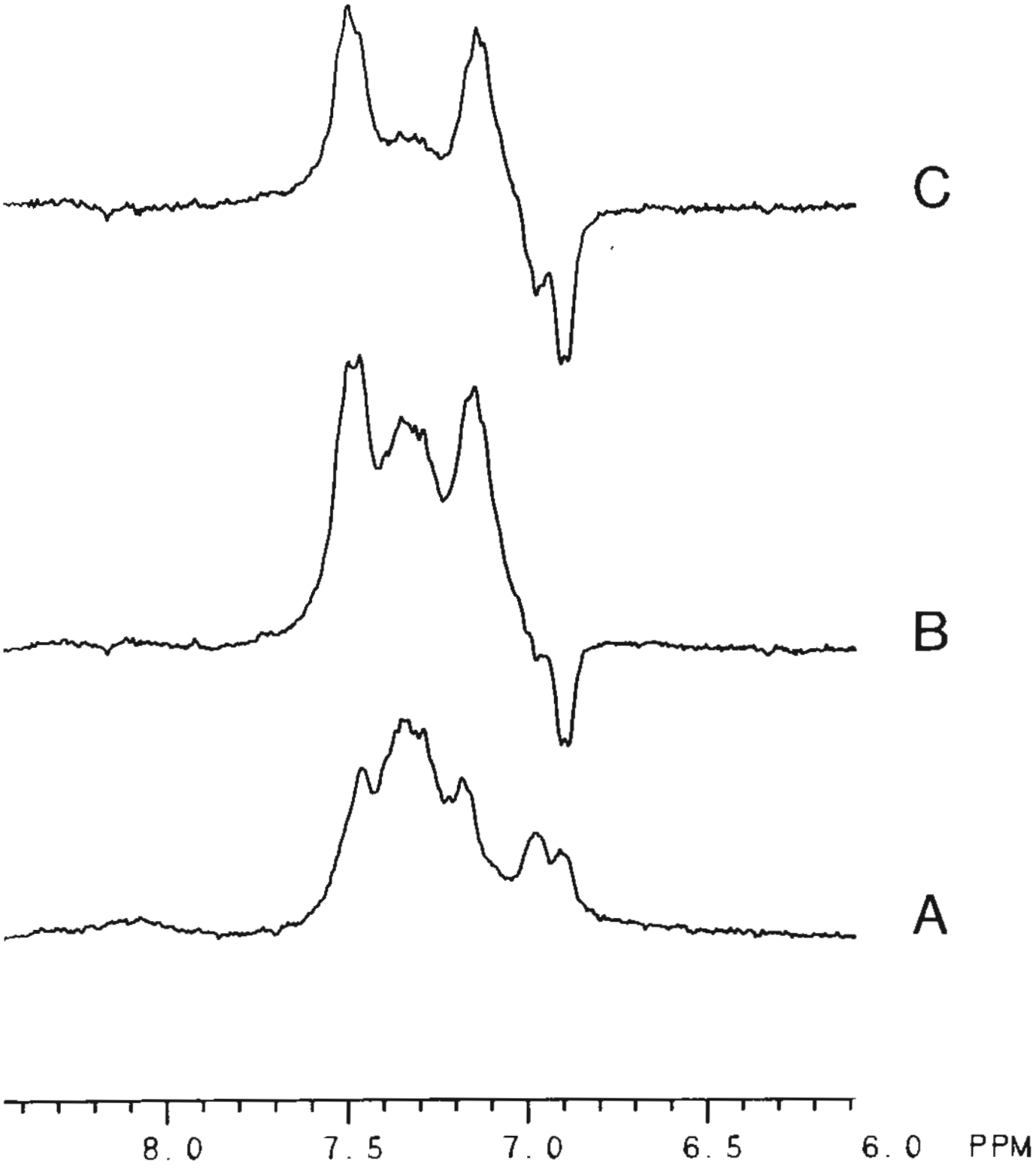
5 mm 1H PHOTO-CIDNP on a NICOLET 300 MHz W.B. Spectrometer

In response to your request we would like to tell you about the renewal of interest in the laser induced PHOTO-CIDNP experiment on a NICOLET 300 MHz W.B. Spectrometer.

Since we sold our BRUKER 270 MHz spectrometer we have not been able to perform this experiment. However, we recently modified our 300 MHz for this purpose. Jonathan Tyler from our Biomedical Design Centre, designed and built a fibre optic pathway. This connects a Spectra Physics argon ion laser model 164 operating in the multiline mode to the probe using a bottom entry approach into the magnet. The light beam is transmitted and modulated by way of this network which consists of a shutter, beam reducer, 500 μm fibre optic cable, beam collimator and expander to a 5 mm flat bottom tube containing a 330 μl sample. A TTL level gating pulse from the 293 c pulse programmer is used to control the shutter.

We are using the photo-CIDNP experiment to monitor the exposure of aromatic residues in proteins. The accompanying figure shows some preliminary results obtained with detergent solubilized M13 coat protein, a small integral membrane protein which contains two tyrosine residues, one tryptophan and no histidines. The protein was 2.5 mM in 10 mM sodium dodecylsulphate-d_{25}, 5 mM sodium borate pH 9.0, 90 mM sodium chloride and 0.1 mM 3-N-carboxymethyllumiflavin. Light and dark spectra were obtained alternately and stored in adjacent blocks of memory; a 20s delay was left between transients to avoid heating artifacts. (A) Dark spectrum (aromatic region only), 16 transients; (B) light spectrum, 16 transients, with illumination for 1s at a laser power of 3W; (C) difference spectra, showing both tyrosine emission and tryptophan absorption.

Gerry McQuaid Gillian D. Henry Brian D. Sykes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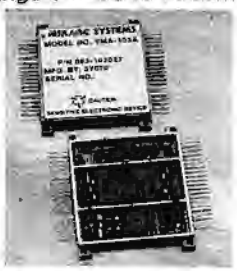

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Texas A&M University NMR Newsletter - Book Reviews

Book Review Editor:
William B. Smith, Texas Christian University, Fort Worth, Texas.

" Carbon-13 NMR Spectroscopy "

by

Hans-Otto Kalinowski, Stefan Berger, and **Siegmar Braun.**

John Wiley & Sons, Inc., New York, U.S.A.;
765+ pages; 1988.

This is an updated (May, 1986) translation, by Jack K. Becconsall, of the German version originally published in 1984 by George Thieme Verlag. The target audience is composed of organic chemists engaged in research, including graduate students, who will probably find it somewhat expensive at *ca.* $150. For libraries and more established researchers, however, it is well worth the investment.

Two introductory chapters cover the theory and techniques of NMR. The latter aspect is restricted to pulse FT methods, and includes sufficient detail to permit the reader to keep up with the ever-increasing number of new pulse sequences. The major ones known through the end of 1985 are specifically discussed.

The next two chapters, which total 530 pages, constitute the heart of this book. They cover the relation of chemical shift to structure, arranged by compound class, and the relation of structure to ^{13}C-X spin-spin coupling, arranged by the coupled nuclei and by the number of intervening bonds. Many specific examples are given, as well as correlation rules and equations.

The book concludes with four short chapters on relaxation phenomena, dynamic NMR, shift reagents, and the use of C-13 NMR in the determination of reaction mechanisms. In addition to excellent separate indices for specific compounds and general subjects, four appendices for answers to problems, a general bibliography, information systems, and abbreviations and acronyms are included.

As stated above, this book would be a valuable addition to the library of any organic chemist engaged in research. Its major competition for the tight book dollar would be the third edition of the classic of the same title by Breitmaier and Voelter (VCH Publishers). These books are more similar than they are different, as reflected in their publication dates, coverage, and cost. The major differences are that the book being reviewed here includes over 100 excercises, and that it provides a much more extensive collection of chemical shift data for the basic classes of organic compounds. On the other hand, the coverage of chemical shift data and correlations for natural products is much more comprehensive in the Breitmaier and Voelter book. These differences obviously reflect the preferences of the authors and could be a factor in the selection of one or the other book by prospective purchasers.

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TEXAS A&M UNIVERSITY

NMR NEWSLETTER

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Postdoctoral Position. Available January 1, 1990 to study molecular biophysics of model bile and glyceride digestion systems. Require Ph.D. in chemistry or biochemistry, with experience in one or more of the following areas: NMR (multinuclear, spin relaxation, 2D, magic-angle spinning techniques), quasielastic light scattering, enzyme kinetics, lipid biochemistry. Send resume and two letters of recommendation to Dr. Ruth E. Stark, Department of Chemistry, City University of New York, The College of Staten Island, 50 Bay Street, Staten Island, N.Y. 10301. EO/AA Employer.

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CSI 2T Applications

Shielded Gradients: Theory and Design

NMR imaging and localized spectroscopy depend on the use of pulsed magnetic field gradients. As these techniques have grown more complex, it has become apparent that eddy currents created in the magnet cryostat and other structures by pulsed gradients have become the chief limitation to many sophisticated applications.

Figure 1a illustrates the design problem for unshielded gradients. Figure 1b illustrates the shielded gradient arrangement. Figures 2 and 3 show the contours of constant flux for an unshielded and shielded Z gradient coil, respectively. This demonstrates that, for the shielded gradients, most of the flux has been kept away from the magnet bore.

The dramatic reduction of eddy currents which can be made over the conventional, unshielded gradients is shown in Figures 4a, b. These graphs show frequency as a function of time following the application of a long, constant amplitude gradient pulse which is suddenly cut off. Soon after cut off, a 90° pulse is applied and the complex FID recorded. The instantaneous frequency is then obtained from the FID and normalized by dividing by the frequency offset at the sample during the gradient pulse.

Figure 4a shows a typical decay of extra magnetic fields in a CSI 2T instrument caused by eddy currents in the conventional, unshielded gradient set with compression.

Figure 4b shows the decay of the uncompensated shielded Z gradient and Figure 4c shows the Z gradient decay with compensation. Note that the time scale for 4b and 4c is five times shorter than that for the unshielded gradients.

Fig. 1a.

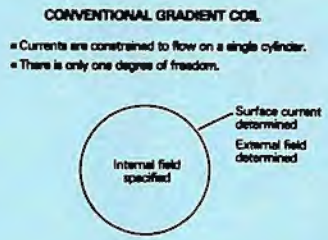


Fig. 1b.

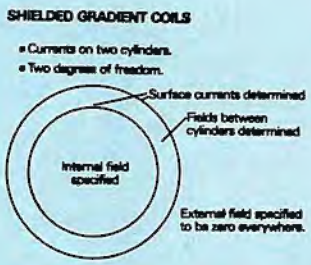


Fig. 1a—Design problem for unshielded gradients. The field inside the winding is specified to be a linear gradient and the current pattern on the cylinder is determined. ***Fig. 1b****—Design arrangement for shielded gradients. The field inside the inner cylinder is specified to be a linear gradient and the field beyond the outer cylinder is specified to be close to zero. The current patterns on both inner and outer cylinders are then determined.*

Fig. 2.

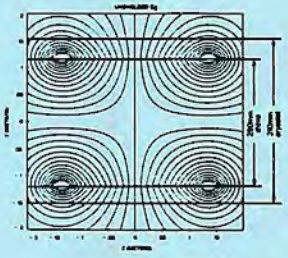
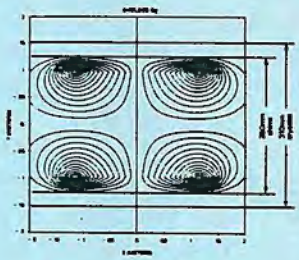


Fig. 3.



Lines of constant flux for Z-gradient. ***Fig. 2****—Unshielded gradient. Note that flux lines extend well beyond the cryostat bore.* ***Fig. 3****—Shielded gradient. Flux lines are kept within the outer gradient cylinder.*

Fig. 4a.

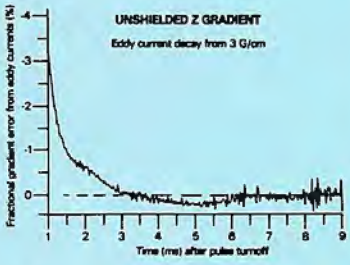


Fig. 4b.

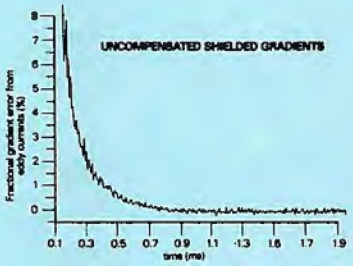
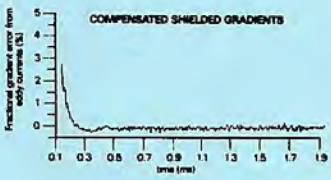


Fig. 4c.



Decay of field following application of square gradient pulse. ***Fig. 4a****—Unshielded gradients.* ***Fig. 4b****—Shielded S150 gradient with no waveform compensation.* ***Fig. 4c****—Shielded S150 gradient with waveform compensation.*

GE NMR Instruments

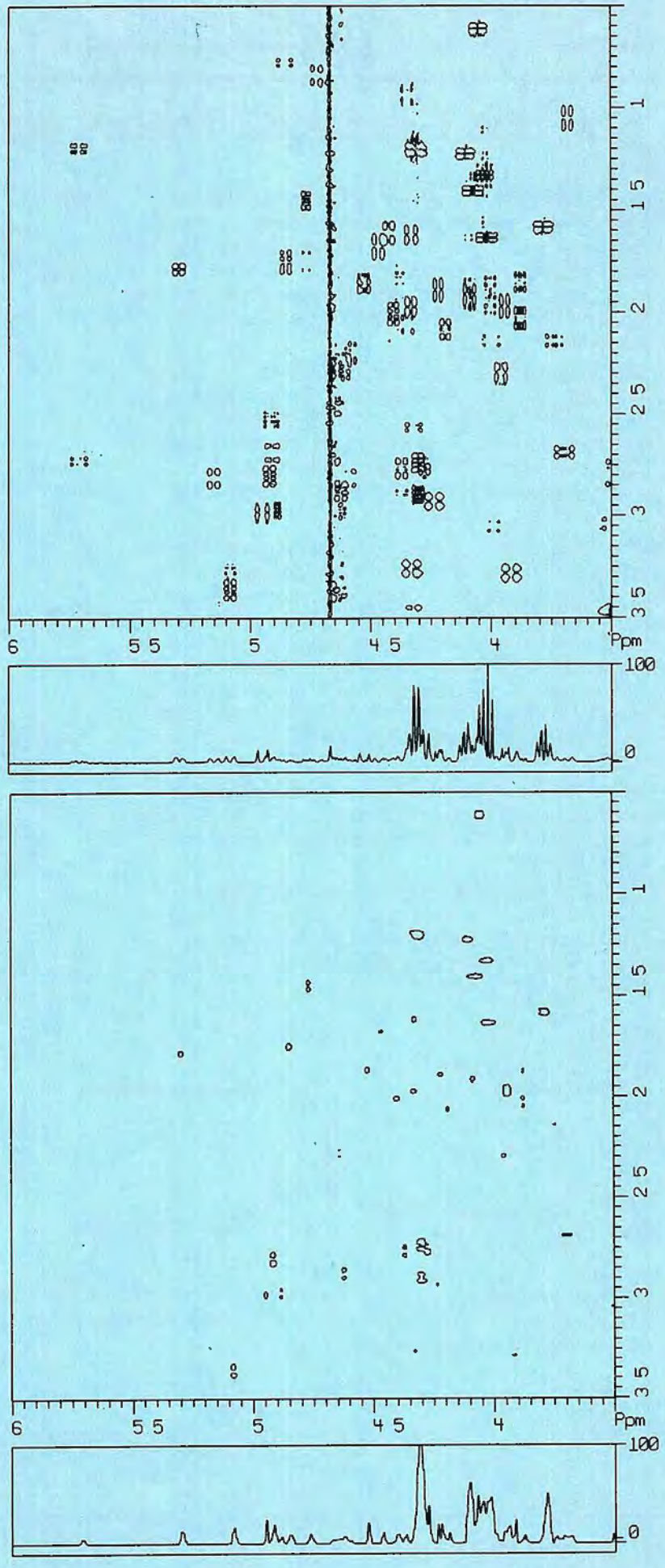
VPLX

A GSX UPGRADE

JEOL USA introduces the VPLX data processing package, our latest upgrade to the GX and GSX NMR spectrometers. When used with the latest network options of Multi-PLEXUS, VPLX provides the power and speed of a VAX™ and eliminates the need to learn a new set of software commands.

In addition to allowing for off-line processing, VPLX offers advanced functionality such as MEM/LPZ and Symmetry Filtering. The top data shows the normal NH to alpha region in a double quantum filtered COSY of BPTI in water. This matrix was produced on a GSX-400, processed on VPLX, and printed on a laser printer. The bottom data is identical to the first with the exception that a symmetry filter has been applied to the matrix. This symmetry filter discriminates on the basis of the known phase relationship of true COSY peaks. Each of the COSY peaks that passes through the filter is reduced to a centroid representation.** This filtering allows for the rapid elimination of spurious cross peaks and is the first step necessary for computer based spectral interpretation.

For more information, contact JEOL.



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*VAX is a trademark of Digital Equipment Corporation
**JC Hoch, S Hengyi, M Kjaer, S Ludvigsen, and FM Pousen, "Symmetry Recognition Applied to Two-Dimensional NMR Data", Carlsberg Res., Commun., Vol. 52, p.111, (1987).